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POLYOLEFINS
RECENT IMPROVEMENTS
APPLICATIONS AND COMPARISONS

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Secretariats European sections

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SPE -North Sea Delta Section
c/o MPMI
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SPE -Scandinavia
P.O.B. 91
DK-1003 COPENHAGEN

SPE -SWITZERLAND
Dr Th. Schwyn (V.K.I.)
P.F. 300
CH-8035 ZUERICH

S.P.E. International
Mr. R. Forger
656 West Putnam Avenue
Greenwich, Conn. 06830
U.S.A.

OPENING REMARKS

EURETEC '79

June 14, 1979 Gent, Belgium

Joe Magliolo

It is indeed an honor and a pleasure for me to participate in the first EURETEC, and I want to add my thanks and congratulations to Dr. Cornet, Dr. Morand, Mr. De Craene, and to the other members of the committees for putting together such a fine meeting.

This morning I have been asked to speak a few minutes about SPE.

SPE is an International Organization with 21,000 members world wide, and it has its headquarters in Greenwich, Conn. Many of you may know that for the past few years we have been operating under the influence of the Long Range Plan which was conceived and organised by Past President Dr. Larry Broutman. This is the document being used for future planning, and this plan calls for membership to reach over 28,000 in 1983.

SPE is currently composed of 76 sections and 15 divisions. Sections are comprised of specific geographical territories such as: Chicago, Southern California, France or Norht Sea Delta . Divisions are devoted to specific technical disciplines such as Vinyl Plastics and Plastics Analysis. The sections throughout the world are located in this manner: 66 in the U.S. and Canada; 5 in Europe; 3 in the Middle and Far East and 2 in Mexico.

SPE affairs are governed by a Council, or Parliament, which contains a councilman from every Section and Division in the world. This council meets 3 times a year. The SPE Executive Committee conducts and administers activities throughout the year including work by all committees. The SPE Exicutive Committee is composed off 12 volunteer members and the Executive Director, Bob Forger. SPE Officers are elected by council in the election meeting which normally takes place in February.

The charter, or objective of the Society is "To promote the Scientific and Engineering Knowledge Relative to Plastics". How is this done? Much of it is done by meetings such as the Euretec. The largest SPE meeting held each year is the ANTEC, or Annual Technical Conference. In 1978 the meeting was held in Washington D.C., and the 1979 meeting was held last month in New Orleans, La. I know some of you attented the Washington meeting last year and Dr. Kepes attended both meetings, and both were succesful with over 3000 attendees each. In fact a new record for attendance was set at New Orleans with over 3500 attendees In both meetings over 200 papers presented in 7 simultaneous sessions. All ANTEC's have a general theme, and the theme of the New Orleans meeting was "PlasticsEfficient Use of Resources". However, all ANTEC's contain many topics and many technical disciplines. Evidence that the meeting is international in nature is pointed out by the fact that there were papers presented by people from 14 countries.

Since this is the largest meeting and the biggest single SPE event each year, the Executive office at Greenwich is heavily involved in planning and arrangements. The professional staff works with two committees called the Operating Committee and the Technical Program Committee. These are similar to the committees who have worked on the EURETEC.

The ANTEC, then, is the biggest single event in which SPE "Promotes the Scientific and Engineering Knowledge relative to Plastics".

The second National meeting is called NATEC, or National Technical Conference, and it is normally about 15 - 30 % the size of ANTEC's. Our last NATEC was held in Chicago in November of 1978. It was composed of two topics - Plastics in Packaging and Acrylonitrile. There were 514 attendees and 55 papers presented. The meeting in 1979 will be held in Detroit, Michigan, in November and the topic will be Plastics - The answer to Transportation in the 80's. Since NATEC is also a national meeting the professional staff again is heavily involved and works with the volunteer Operating and Technical Program Committees.

The largest number of Technical meetings presented each year are RETEC's, Regional Technical Conference, and DIVTEC's, Divisional Technical Conference. In the current year 6 RETEC's and DIVTEC's were presented. There were a total of 1400 attendees which compares with the over 4,000 attendees for ANTEC and NATEC. To this total the seminar activity should be added. There were 86 seminars with 1542 attendees. Therefore, almost 3000 registrants attended individual meetings and this coupled with the National Meeting comes to a total of over 7,000 attendees.

Incidently this was a rather slow year for RETEC's and DIVTEC's, and we anticipate much more activity in the upcoming year.

Most RETEC's are conducted by one section and it is normally on one topic. Divisions may choose either to put on a DIVTEC which is their specific technical discipline or to put on a RETEC in collaboration with a section. There are times when it is advantageous for sections to join together to put on a RETEC. This is the case in the Western United States where PACTEC's (Pacific Technical Conference) are put on. California and the Western U.S. in an area quite different from the remainder of the U.S., and the meetings are tailored to meet the needs of that region.

This first EURETEC is an excellent example of cooperation between sections which cross several National Boundaries in the U.S. We think a fantstic job has been done.

I would like to say a few words about the subject of the Symposium - "Polyolefins, Recent Improvements - Applications and Comparisons". For me this is an excellent subject since my home section - The South Texas Section - is in the area where most of the Polyolefins in the U.S. are produced. The South Texas Section has put on two RETEC's called "Polyolefins I - what's new in Polyolefins" and "Polyolefins II - Processes, Products and Processing". Certainly, we can all agree that the whole world is interested and concerned about Polyolefins since Polyolefins are such a large share of the world's Plastics production.

And certainly your theme - "Recent Improvements, Applications and Comparisons" in one which is in tune with the times and one which precisely fulfills the purpose of SPE - "To Promote the Scientific and Engineering Knowledge Relative to Plastics".

Again thank you for giving me the honor of being the first Honorary Chairman of the First EURETEC and I'm very proud to be here to bring you congratulations for having such an outstanding meeting.

First Euretec
GENT
June 14-15 1979

Polyolefins, Recent Improvements
Applications and Comparisons

ECONOMIC TRENDS IN WORLD POLYOLEFINS

DEVELOPMENT AND COMPETITION

Françoise Pardos-Jacques

First Vice President SPE-France

Pardos Marketing
"Beau-Voir" Bures
78630 Orgeval
France
Tel: (1) 975 80 19

Polyolefins are one of the oldest, and the largest group, of plastics, accounting for about 38% of total world production-consumption of plastics of all kinds. Out of an estimated total of plastics in the world of 47 million tons in 1978, polyolefins account for about 18 million tons, of which LDPE 10 million tons, PP 4 million tons, HDPE 4 million tons. Since it is still difficult to gather detailed estimates of plastics production-consumption throughout the whole world, including countries of the Eastern block and most of the Third World, comparisons will be limited to the three best-known areas, United States, Japan and Western Europe.

World production of plastics, 47 million tons of which:

USA	16.2 million tons
Germany	6.9
Japan	6.4
USSR	3.4
France	2.9
Italy	2.7
UK	2.7
Spain	1.1
others	4.7
Total	47

Since not all official 1978 figures were yet found, comparison of total polyolefin volume versus other plastics is made for 1977, for better consistency.

Plastics¹⁾ consumption²⁾ in 1977

in the three largest "established" areas
in thousands of metric tons

	<u>W. Europe</u>	<u>United States</u>	<u>Japan</u>	<u>Total 3 areas</u>
LDPE	3 300	2 654	950	6 904
HDPE	1 190	1 420	470	3 080
PP	840	1 106	720	2 666
(Total 3 major polyolefins)	(5 330)	(5 180)	(2 140)	(12 650)
PVC	3 260	2 270	1 475	7 005
PS and copolymères	1 855	1 926	1 015	4 796
PUR	730	811	130	1 671
Reinforced polyester	340	370	143	853
Thermoset molding powders	270	206	160	636
Engineering plastics	320	320	110	750
All other "solid" plastics	295	417	227	939
Total "solid" plastics	12 400	11 500	5 400	29 300

1) Only "solid", three-dimensional plastics, exclusive of liquid resins
for paints, varnishes, glues, adhesives.

2) Excluding exports to other areas of the world.

Out of a total of 29 million tons of "solid" plastics, to be converted into
three dimensional objects, in the three largest "established" areas,
polyolefins amounted to 12.6 million tons in 1977, or 43% of total "solid"
plastics.

LDPE and PVC are about equal in volume in this area, with 7 million tons,
then HDPE and PS, with about 3 million tons each, then PP growing faster
and getting close to 3 million tons as well.

For a more detailed analysis only the seven largest producing countries
in Western Europe have been retained for the study, Germany, France,
the UK, Italy, Benelux countries and Spain.

LDPE Production

	<u>USA</u>	<u>Western Europe 7 countries</u>	<u>D</u>	<u>F</u>	<u>UK est.</u>	<u>I</u>	<u>B</u>	<u>NL</u>	<u>S</u>	<u>Japan</u>
1970	1 837	2 008	438	352	317	354	200	280	67	820 est.
1971	2 032	2 268	490	420	307	405	230	336	80	850 est.
1972	2 372	2 269	550	486	375	470	310	385	93	936
1973	2 264	3 144	710	636	400	550	325	420	103	985
1974	2 729	3 408	800	713	420	550	320	460	145	1 209
1975	2 148	2 486	550	480	313	430	215	360	138	868
1976	2 620	3 410	750	688	400	620	230	475	247	805
1977	2 949	3 542	770	715	362	660 est.	240	490	305	807

LDPE Consumption

1970	1 673	1 542	400	284	275 est.	303	78	77	125 est.	700 est.
1971	1 896	1 762	460	330	296	350	90	85	151	750 est.
1972	2 208	2 086	570	383	330	410	106	95	192	781
1973	2 461	2 584	710	463	390	515	125	111	220	900
1974	2 547	2 525	720	485	390	470	132	113	215	862
1975	2 005	2 185	650	397	350	400	110	93	185	731
1976	2 366	2 664	710	490	420	550	130	115	249	614
1977	2 688	2 797	730	520	425	580	140 est.	120	282	598
				550						

HDPE Production

1970	746	660	380	58	67	89	30	27	9	380 est.
1971	855	758	430	84	66	95	37	35	11	430 est.
1972	1 062	936	500	121	66	120	50	45	34	483
1973	1 254	1 174	660	149	70	125	57	67	46	612
1974	1 217	1 280	700	187	70	140	60	70	53	636
1975	1 048	1 041	520	143	70	135	65	55	53	354
1976	1 421	1 365	680	226	70	168	80	75	66	436
1977	1 617	1 428	673	239	70	190 est.	90	72	94	496

HDPE Consumption

1970	643	475	200	85	50 est.	70	23	27	20 est.	245
1971	735	556	225	95	58	85	28	31	34	255
1972	930	684	250	125	76	100	35	35	63	306
1973	1 134	843	310	148	96	115	46	40	88	451
1974	1 121	869	330	157	99	110	48	40	85	406
1975	948	770	270	148	92	95	45	40	80	309
1976	1 255	967	340	183	123	125	54	44	98	305
1977	1 423	1 027	345	182	135	130 est.	56	53	126	317

PP Production

	<u>USA</u>	<u>Western Europe 7 countries</u>	<u>D</u>	<u>F</u>	<u>UK</u>	<u>I</u>	<u>B</u>	<u>NL</u>	<u>S</u>	<u>Japan</u>
1970	452	286	65	20	74	88	-	22	17	470 est.
1971	558	320	70	25	90	90	-	24	21	550 est.
1972	766	417	100	39	118	110	-	30	20	618
1973	978	563	130	48	160	160	-	45	20	963
1974	1 001	682	150	74	205	170	-	55	28	792
1975	861	550	135	49	170	130	-	40	26	594
1976	1 153	850	240	75	240	200	10	55	30	669
1977	1 226	996	250	91	245	215	84	72	39	608

PP Consumption

1

1970	415	258	58	27	85	57	5	8	18	380 est.
1971	520	293	67	32	98	65	6	10	15	460 est.
1972	668	365	80	45	127	75	7	12	19	491
1973	848	487	120	60	160	100	8	16	23	576
1974	901	529	115	80	176	100	9	18	31	611
1975	768	497	110	75	156	95	14	18	29	557
1976	992	663	165	95	190	130	19	25	39	537
1977	1 098	745	190	106	196	140	34	30	49	507

1 plastics only, excl. textile fibres.

Comparative end-use analysis in the United States and the seven largest European markets

Again taking the year 1977 as a base, the overall size of the three polyolefin market and its split by end-uses can be compared.

The LDPE total market is of about the same size in the US and in the seven largest markets in Europe, although the application breakdown differs. The comparison of end-uses between these two areas indicates that the European consumption of HDPE is larger than in the US in markets where this plastic has successfully replaced paper, like heavy duty bags, shopping bags, shrink film, while the reverse is true in extrusion coating where LDPE is associated with paper. The simple explanation to this is the cheaper price of paper and board in the United States which prevented larger inroads of HDPE into these traditional paper markets.

Comparisons of other applications are not as significant.

Comparative breakdown of LDPE end-uses
in the US and 7 largest markets
in Western Europe 1977
 (in thousands of metric tons)

	<u>USA</u>	<u>7 countries</u>	<u>D</u>	<u>F</u>	<u>UK</u>	<u>I</u>	<u>B</u>	<u>NL</u>	<u>Spain</u>
<u>Film, total</u>	1 663	2 007	539	318	305	450	105	107	183
heavy duty bags	59	290	87	47	35	35	26	20	40
shopping bags	79	169	65	14	13	50	7	5	15
refuse bags	308	274	38	22	35	120	9	25	25
shrink and stretch	86	269	95	45	38	55	8	10	18
laminates	n.a.	56	12	13	7	10	2	4	8
agriculture	48	150	35	45	6	35	6	8	15
building	77	89	18	12	24	10	9	6	10
other uses	916	710	189	120	147	135	38	29	52
Extrusion coating	217	102	29	22	15	15	6	7	8
Wire and cable	184	168	32	65	22	18	7	7	17
Blow molding	25	109	18	9	10	25	1	8	38
Pipes and profiles	12	47	5	24	-	7	5	2	4
Injection molding	273	250	52	70	30	45	12	13	28
Other uses	314	129	45	12	43	20	4	1	4
Total	2 688	2 812	720	520	425	580	140	145	282

HDPE consumption is relatively smaller in the seven countries of Europe, than in the United States. The application breakdown is different too, with injection molding still relatively more important and less diversified in Europe, with a substantial amount in handling and packaging crates. This again gives hints of the good resistance of corrugated cardboard to plastic inroads, in the United States. Pipes and profiles are relatively small in Europe, as well as wire and cable.

Comparative breakdown of HDPE end-uses
in the US and 7 largest markets
in Western Europe 1977
 (in thousands of metric tons)

	<u>USA</u>	<u>7 countries</u>	<u>D</u>	<u>F</u>	<u>UK</u>	<u>I</u>	<u>B</u>	<u>NL</u>	<u>Spain</u>
							<u>1976</u>		
Injection molding	310	400	114	78	24	75	20	34	55
of which (crates)	(45)	(183)	(44)	(51)	(7)	(30)	(11)	(10)	(30)
Blow molding	571	458	170	85	67	45	29	17	45
Pipes and profiles	196	51	18	6	13	1	2	5	6
Wire and cable	45	6	n.a.	5	1	n.a.	n.a.	n.a.	n.a.
Monofilaments	n.a.	19	n.a.	1	n.a.	3	1	n.a.	14
Films	62	60	18	8	18	4	6	3	3
Other uses	239	39	20	2	12	2	2	1	
Total	1 423	1 033	340	185	135	130	60	60	123

The application breakdown of PP is fairly similar in Europe and in the United States with a still fairly important gap in overall tonnage, per capita consumption of PP being currently 3 kg compared with 5.5 kg in the United States.

Comparative breakdown of PP end-uses
in the US and 7 largest markets
in Western Europe 1977
(in thousands of metric tons)

	<u>USA</u>	<u>7 countries</u>	<u>D</u>	<u>F</u>	<u>UK</u>	<u>I</u>	<u>B</u> <u>1976</u>	<u>NL</u>	<u>Spain</u>
Injection molding	450	348	100	65	70	75	10	12	16
Split film	345	216	32	28	70	30	18	15	23
Monofilaments	n.a.	26	9	2	5	5	1	-	4
Film	93	101	27	8	37	20	2	5	2
Pipes and profiles	7	16	9	1	3	2	1	-	-
Blow molding	23	5	-	-	2	3	-	-	-
Other	180	26	3	2	9	5	2	1	4
Total	1 098	738	180	106	196	140	34	33	49

Polyolefin consumption forecast

Demand for LDPE has not increased very much in the three "established areas" between 1973-74 and 1977. 1978 has been a little better, about 4-5 % over 1977.

Performance is a little better for HDPE consumption which is enjoying strong markets with blow molding and film, although from a still small volume.

PP on the contrary has enjoyed a continuous 11 % annual growth in Western Europe, in the seven countries under study.

Some extrapolation has been attempted for the three polyolefin markets in various areas of the world. Western Europe is taken as a whole and "other world" includes both Eastern and Third worlds.

The rates may appear conservative compared to a number of other forecasts. However the last five year history has shown how difficult it may be to some markets and country consumption to keep a sustained growth of more than 3 %, over a seven-year span, now that the main inroads of plastics into "traditional" materials have been achieved and that a pervasive saturation has been reached in most packaging and durable goods applications in the industrialised countries.

The aggregate results of these forecasts are shown in the following table :

Polyolefin consumption
(in thousands of metric tons)

	<u>1978</u>	<u>1982</u>	<u>1985</u>	<u>average annual growth rate %</u>
<u>LDPE</u>				
Western Europe	3 400	3 830	4 200	3
USA	2 800	3 150	3 500	3
Japan	600	650	700	2
Other world	3 200	4 500	5 800	9
Total	10 000	12 130	14 200	5.2
<u>HDPE</u>				
Western Europe	1 400	1 650	1 840	4
USA	1 600	1 800	2 000	3
Japan	300	340	370	3
Other world	700	920	1 130	7
Total	4 000	4 710	5 340	4.3
<u>PP</u>				
Western Europe	1 050	1 600	2 200	11
USA	1 200	1 450	1 670	5
Japan	550	670	780	5
Other world	1 200	2 100	3 200	15
Total	4 000	5 820	7 850	10
World total 3 major polyolefins	18 000	22 660	27 390	6.1
World total plastics, all types	47 000	57 000	66 000	5 %
% of polyolefins in total plastics	38 %	40 %	41.5 %	

The growth thus forecast will not be even throughout various applications of polyolefins.

LDPE markets are closely linked to film, with irregular development depending upon applications. Thus LDPE film, at least in industrialized countries, will be stagnant in heavy duty bags, shopping bags, and small bags, while demand will continue to grow everywhere for refuse bags, shrink and stretch film, laminates and film for agriculture.

HDPE will grow mainly in blow molding, particularly large containers for which there is no other plastic as suitable. Other blow molding applications to develop are gasoline tanks in automobile, which might be competing with PP, and small containers for paints and other products. Although it will never be a sizable market, tubing might develop for gas carrying.

The growth of PP will be the fastest. However PP is not likely to overtake LDPE in the foreseeable future, in spite of its faster growth rate. Of the three major polyolefins, it is HDPE which is most likely to suffer from PP rapid development, particularly in injection molding. Forthcoming large applications of PP include film, as replacement of cellophane, moldings of all kinds, competing with PS, ABS, HDPE and even some engineering plastics, when properly filled or reinforced, tubing for hot water and liquids, substituting to steel, and fibers to replace natural materials such as sisal, a well as synthetics such as PA and acrylics.

Capacity and actual production

Although much is repeatedly said and written about the continuing low operation rate of existing and future production capacity, particularly for PP, this prevailing concern must be somewhat tempered if not entirely waived :

- When adding up new forthcoming capacity and projects, it is customary to add firm construction projects and studies alike. It is certain that not all announced projects will materialize, or that they will at a later date than initially indicated, while other projects, larger or smaller may also be announced.
- Even more importantly, all additions of future capacity always neglect subtracting plants which have become obsolete and are to close down. A number of LDPE plants particularly have been operative for many years, and the new polymerization processes point out to the surge of a "second generation" plant building.
- Finally, name plate capacity is a far cry from actual operative capacity.

All these facts must be kept in mind when extreme worries about "glut", "surpluses" are expressed. There still are worrying aspects however, particularly in the largest countries of Western Europe which are to be increasingly exposed to growing competition from :

- new producing countries in Europe, Spain, Portugal, Greece, Scandinavia
- Eastern Europe, as results of buy-back deals or as plain dumping
- oil countries of the Middle East, Saudi Arabia, Kuwait, of which a good third of the forthcoming production will go to Europe.

At the same time, sales from Europe to overseas markets will gradually decrease because of new capacity installed in these areas.

In the longer run, a different share of producing capacities and markets might evolve, the bulk of the main-produced plastics such as polyolefins being increasingly produced where they are to be used in the fast-emerging markets throughout the whole world.

Additional capacity under study and construction
at various dates to 1985
 (in thousands of metric tons)

	<u>LDPE</u>	<u>HDPE</u>	<u>PP</u>
Western Europe	2 500	1 000	1 050
USA	650	260	900
Japan	300	-	300
Other world	<u>4 350</u>	<u>2 540</u>	<u>1 650</u>
Total	7 800	3 800	3 900
1985 estimation total capacity	20 000	9 000	10 000
1985 forecast consumption	14 200	5 350	7 850

LOW DENSITY POLYETHYLENE

Henri BOIS

Chef du Service Assistance Technique
Applications Thermoplastiques

CdF Chimie (F)

SATRAP
Assistance Technique
B.P. 9 - 62670 Mazingarbe

SOCIETY of PLASTICS ENGINEERS

First EURETEC

Gent

June 14-15, 1979

at a national level of our economic preoccupations often tend to hide the present and future evolutions of the plastics market. This is even more confirmed with large commodity products such as low density polyethylene, the main characteristic of which is the existence on a world scale of the law of supply and demand. This if of course correlative with the wide spread commercial export networks of the main producers. but also due to certain properties of the material (impermeability and heat stability) which make long distance transport easier. It is advisable in our analysis therefore to draw attention to the different markets which correspond to this wider perspective and we will distinguish schematically :

- . Technologically advanced countries (eg USA, Europe, Japan)
- . Countries in the process of rapid industrialization (eg Latin America, Taiwan, South Corea)
- . Low developed countries.

1) In technologically advanced countries (we have purposely taken the example of the USA), low density polyethylene over a short period shows quite a good general growth rate (approaching 7% in 78 compared with 77 in the USA) and keeps its preponderant share in packaging and this in spite of saturation in certain sectors of the market. (1)

The growth in high density polyethylene for films is taking place mainly to the detriment of paper rather than to that of low density polyethylene (closer rigidity, and opacity). (2)

Since 1974, following the effects of the energy crisis, a certain awareness has been developing : saving natural resources is becoming one of the constant political components in developed countries. Dealing with technical progress is becoming more a question of knowing how to use it rather than how to achieve it. In the field of plastics an increased importance is thus attributed to the safeguard and wellbeing of the community, health and the environment.

In the film packaging sector (the largest outlet for low density polyethylene) one of the main competitors could well be paper. Well a recent study carried on by a Dutch Institute shows that given identical use (in shopping bags) the energizing consumption to produce 1.000.000 identical articles is 26 tons of petrol equivalent for the polyethylene and 44 tons for the paper - ratio 1 : 1.7).

What's more, it is worth adding that water consumption would respectively be 66.000 and 3.200.000 L (ratio 1 : 48.5). (3)

As for health, one of the essential worries will consist in reducing all possible or hidden noxiousness. If certain plastics seem to be particularly affected although recent progress in fact allows the elimination of manufacturing and degradation residues (catalysts, monomer, additives and so on), the simplicity of its chain, the complete absence of catalytic residues and the excellent stability in the processing of low density polyethylene should enable it to continue being demanded for its perfect innocuity, a consequence of its purity which cannot rival other thermoplastics.

With PVC bottles, disposal plastic bags unfortunately contribute to environmental pollution. Although it is mainly a question of education (for which action by means of the mass media and school information could be envisaged), certain solutions can even now be looked at.

The increase in the photodegradation of polyethylene for example could bring about a faster elimination of refuse without pollution of the earth or. As a matter of fact it finds an application in the mulching of maize where depending of the chosen composition the planning mulching film elimination in the form of dust is possible within a chosen time limit from 30 to 100 days.⁽⁴⁾ The contribution of plastics in general and polyethylene in particular environmental preservation is often less well known. Refuse bags for example, clean and hygienic, enable quickest and quiet refuse collections. Their combustion in incinerators doesn't give out noxious corrosive gases (carbonic gas and water). The consumption of such bags per inhabitant and per kilo, which is already high in certain countries, should increase rapidly in others. (5)

In market terms, in my opinion therefore the low density polyethylene which is suitable for the new politico-economic requirements should not only consolidate its leading position in technologically advanced countries but experience a certain development in new applications, even more so since its performances or its use can still certainly be improved and that the size effect for production, and therefore for prices acts rather in its favour.

As far as I'm concerned the only real problems seem to be of the general economic

- . How will consumption react to the energy crisis ?
- . What will be the nature of the tri-lateral Europe-Japan-USA economic

agreements and the influence of these agreements on the respective customs barriers, and on new production capacities ?

2) In countries going through the phase of rapid industrialization, environmental or energy problems (in so far as certain are petrol producers) are less acut and the emphasis at a national level is put rather on equipment spending. Similarly as a matter of fact the growth in plastics in everyday consumption is experiencing a high increase in percentage if not in volume.⁽⁶⁾ Well, the low density polyethylene is widely used in cabling as an insulator for its dielectric and physical properties on the one hand in telephone cables, and on the other hand in energy cables (from 600V to 60KV) usually in cross-linked form. In this connection a new cross-linking process by silanes (Sioplas-Dow Corning, Monosil) allows one to limit investment since it is no longer necessary as was the case with reticulation by peroxides to operate cross-linking under pressure in long vapor tubes. This saving should be favourable in the development in volume of low density polyethylene in these countries where out-dated equipment does not exist. Similarly the packaging industry, agriculture (small tunnels, mulching, irrigation) are experiencing a high growth rate which can be compared with that of developed countries a few years ago and should constitute solid markets.

3) In low developed countries where the essential problem remains that of the fight against hunger, the United Nations Agencies, the United Nations Organisation for industrial development, FAO is devoted to promoting the use of plastics in agriculture: water reserves, irrigation, mulching, grains silos, protection of citrus fruits (for example films for bananas, etc...). Polyethylene represents a very large proportion of the plastics used in these applications (more than 70%). The main aim which is kept in mind is to preserve either rare natural resources as water or foodstuffs (protection against insects or micro organisms). The intrinsic demand for low density polyethylene in low developed countries should be very high. But this demand is often restrained by monetary restrictions. The absence of a strong currency drastically restricts imports. The example of India is quite typical, for example : one application, the storing of seeds represents a potential of more than 120.000 tons of which the annual loss due to lack of suitable storing facilities is considerable in the double brick buildings of low density polyethylene.⁽⁸⁾ Imports are voluntarily limited by lack of currency in spite of the economic interests of such agricultural solutions.⁽⁶⁾ It is one of the examples where the injection of subsides by industrialised countries would accelerate the depart of the productive investment spiral, creation of profit, creation of investment, and so on, which would allow these countries to take off.

I have spoken to you about the probable development of low density polyethylene. In fact, it concerned low density free-radical polyethylene(FR PE). This precision "free radical" is now necessary since the new processes (for example those of Union Carbide and CdF Chimie)* make it possible to obtain polyethylenes said to be low density by different catalytic processes leading to low density polyethylene Ziegler. The first advantage of these methods is their production cost :

- . At low pressure in fluidized bed for Union Carbide
- . At high pressure but on ordinary equipment of free-radical polyethylene (reactors which are from 250 to 500 times smaller than at low pressure and with considerable adaptability in the quality and the changing of the qualities for CdF Chimie, (9)

Besides this, let's note that these new methods are of course capable of realizing excellent qualities of high density linear polyethylene. What development can we be reasonably led to expect from these new products in low density area ? I don't think that these products are going to displace the traditional polyethylenes because world-wide products do not exist and for example for an identical density, certain properties are not equivalent in films applications, those of the classical low density polyethylene. It is more logically advisable to demand :

What basic fields have been hit by these products ?

- Let's first note that the densities which can be obtained are complementary of the classical densities of usual polyethylene production processes. The CdF Chimie process makes it possible for example to cover the whole range of densities between 0.900 and 0.960 (and therefore corresponding crystallinity). Elasticity modules, and consequently the rigidity, vary correlatively and in line with classical process. The applications made possible by the low (<0.915) and average densities (0.930 d 0.955) are numerous : we must note for example the developments which have already been realized in average densities in rotational moulding sectors or plastic caps.
- the gas impermeability at the same flexibility seems better than that of the classical low density polyethylene.
- The stress crack resistance is generally very good. This explains for example the development trials of these products in cabling (eg : U.S.A.).
- Finally the minimal thickness achievable is very thin (for example 15 microns in grade 2) even for very flexible products which is not possible with the classical industrial methods,

* CdF CHIMIE process as expected started without any problem in March 1979 and is perfectly working.

In summary, I think that, as the majority of main thermoplastics, the "classical" low density polyethylene, i. e. conceived at high pressures by free-radical processes thanks to its wellknown properties (easy transformation, thermic stability, transparence, peroxydes, purity, etc...) should not suffer from other thermoplastics. Only general economic preoccupations (the price of petrol, consequence of consumption) could restrain its development which is still considerable on a world-wide scale, because the uses of this product seem well adapted to to-day's politico-economic preoccupation. Some interesting applications could still be developed by additives notably or by improving certain properties. Unfortunately a wide-spread practice in Europe is for transformers and users not to accept to pay for a supplementary performance (for example, clarity, rigidity, etc...) and this does not encourage the research for special qualities. Some other countries for example the U.S.A. consider it quite normal to pay a bonus for improvement which thus allows plastics research to develop normally. It is easy to conceive the long term risk run by European producers and users if they leave the care of assuring their technological development to others.

Some new methods enable the realization of ionic polymerizations of low density Ziegler polyethylene. In fact, these are new products whose characteristics enable them to be inserted in a complementary way in the usual applications of classical polyethylenes and whose development seems promising.

o o
o

LOW DENSITY POLYETHYLENE

x
PATTERN OF CONSUMPTION

U.S.A.

(1)

MARKET	1000 TONS	
	1977	1978
BLCH MOLDING	25	25
EXTRUSION	217	219
COATING FILM (1.2 MIL AND UNDER)	1663	1773
PIPE AND CONDUIT SHEET (COVER 12 MIL)	12	11
WIRE AND CABLE	13	13
OTHER	184	195
	27	32
INJECTION MOLDING	273	282
EXPORT	261	341
OTHER	274	295
TOTAL	2949	3186
<u>SALE AND USE (1000 TONS) xx</u>		
U.S.A.		
	YEAR	
	1972	2390
	1974	2700
	1975	2160
	1976	2620

xx SPI, compiled by Ernst and Ernst

x Modern Plastics January 1979

U.S.A.

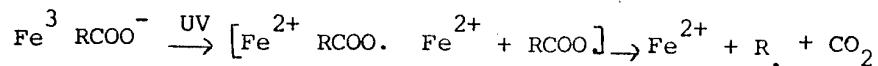
FILE FOR PACKAGING

	1977	1978
POLYETHYLENE HIGH DENSITY	54	70
POLYETHYLENE LOW DENSITY	913	973
POLYPROPYLENE	93	109
POLYSTYRENE	18	20
P.V.C.	76	82
OTHER	40	40
T O T A L	1194	1294

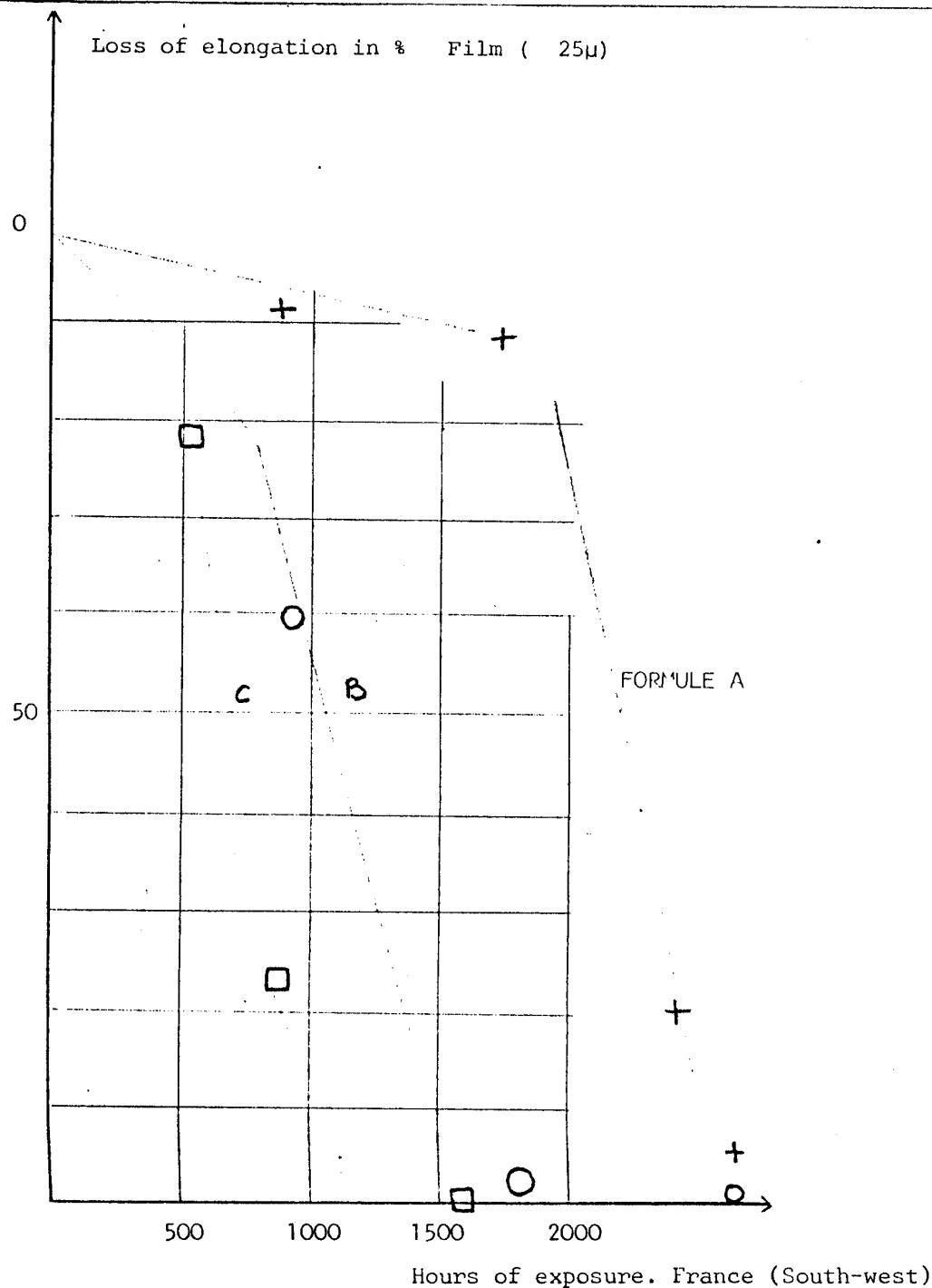
x Modern Plastics, January 1979

SHOPPING BAGS

WEIGHT	21g	30g
VOLUME	12 L	12 L
MATERIAL	PE-film 55μ	Kraft paper 70 g/cm ²
	↓	↓
ENERGY	26 m.t.	44 m.t.
WATER	66.000 l	3.200.000 l



R. = Free radical which starts degradation of the polyethylene



REFUSE BAGS CONSUMPTION IN LD-PE

	CONSUMPTION MT/YEAR			INHABITANTS (MILLIONS)	CONSUMPTION PER INHABITANT KG/YEAR
	1970	1972	1974		
GERMANY	3 000	9 000	15 000	18 000	61
BELGIUM	1 000	5 000	8 000	10 000	10
FRANCE	1 500	6 000.	14 000	28 000	53
ITALY	35 000	60 000	100 000	100 000	56
NETHERLANDS	5 000	13 000	15 000	16 000	14
SWITZERLAND				12 000	6
U.S.A.				260 000	215

CONSUMPTION FORECAST (LD-PE)

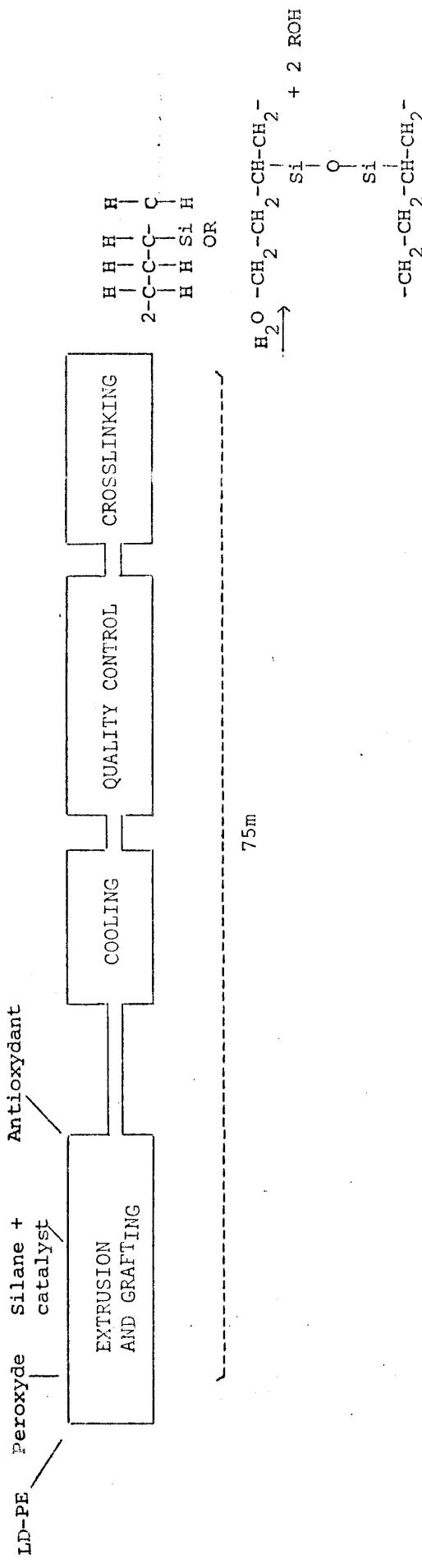
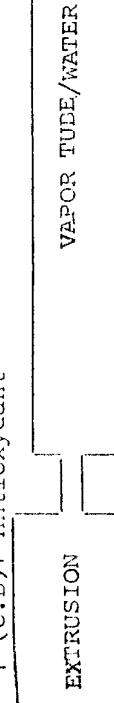
(1000 T)

(6)

AREA	79	80	GROWTH RATE 76-80 (%)	81	82	83	84	85	GROWTH RATE 81-85 (%)
MIDDLE EAST	150	164	13	194	216	240	272	302	12
INDIAN PENINSULA	96	108	15	121	134	152	170	190	12
SOUTH EAST ASIA	200	224	10	244	265	287	312	341	9
FAR EAST	309	344	11	369	393	417	444	469	6
JAPAN	850	890	5	935	980	1030	1080	1130	5
OCEANIA	140	160	12	178	190	202	230	243	9
EAST AND SOUTH AFRICA	133	148	10	160	172	186	201	212	8
ARGENTINA			19	100					
INDIA	70	80	23	90	100	115	130	145	

MONOSIL

(7)

CROSSLINKING BY CONTINUOUS VULCANIZATIONGranules LD-PE + Peroxyde
+ (C.B) + Antioxydant

125m

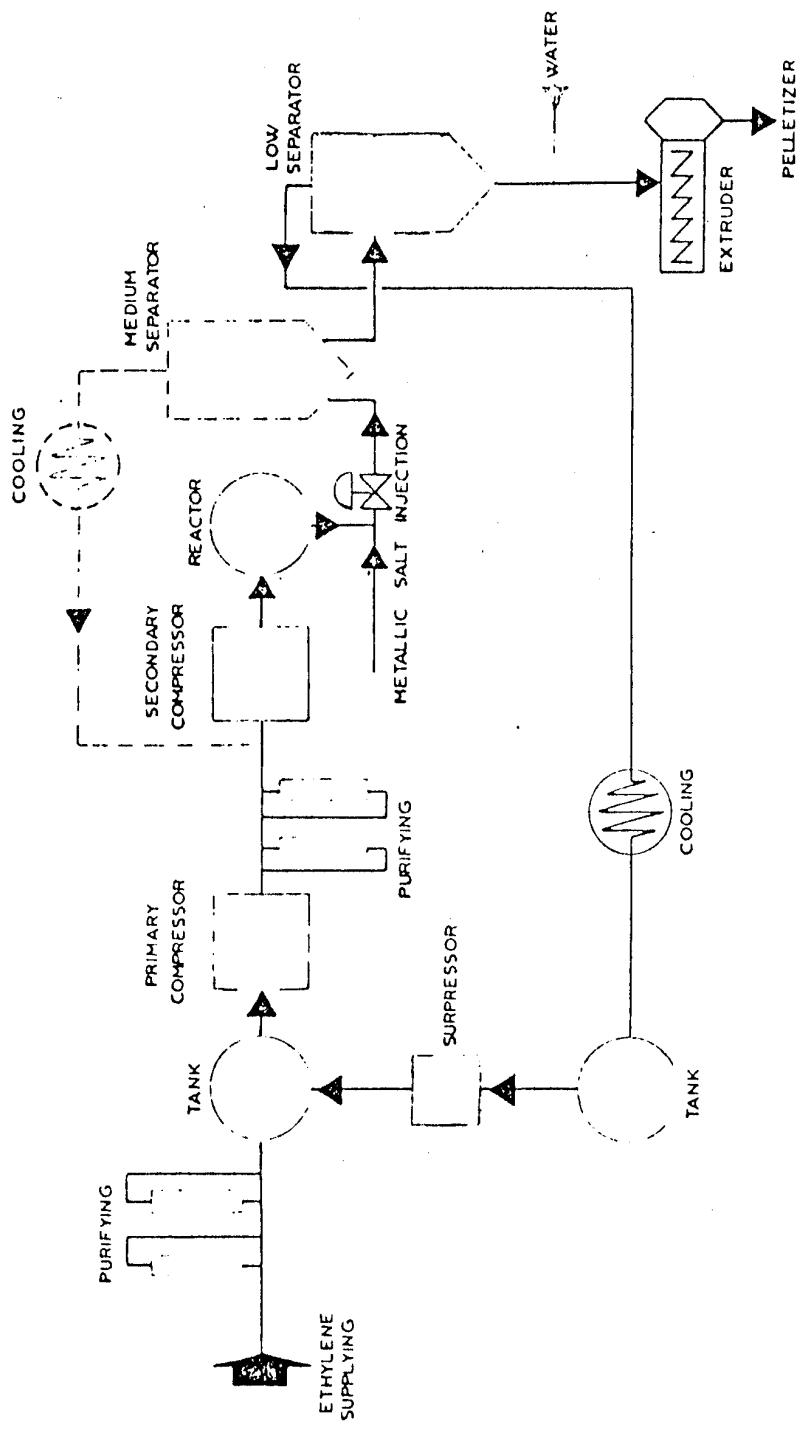
INVESTMENT

250	100
200	
150	
100	
50	80
0	MONOSIL

COST COMPARISON OF GRAIN STORAGE BINS

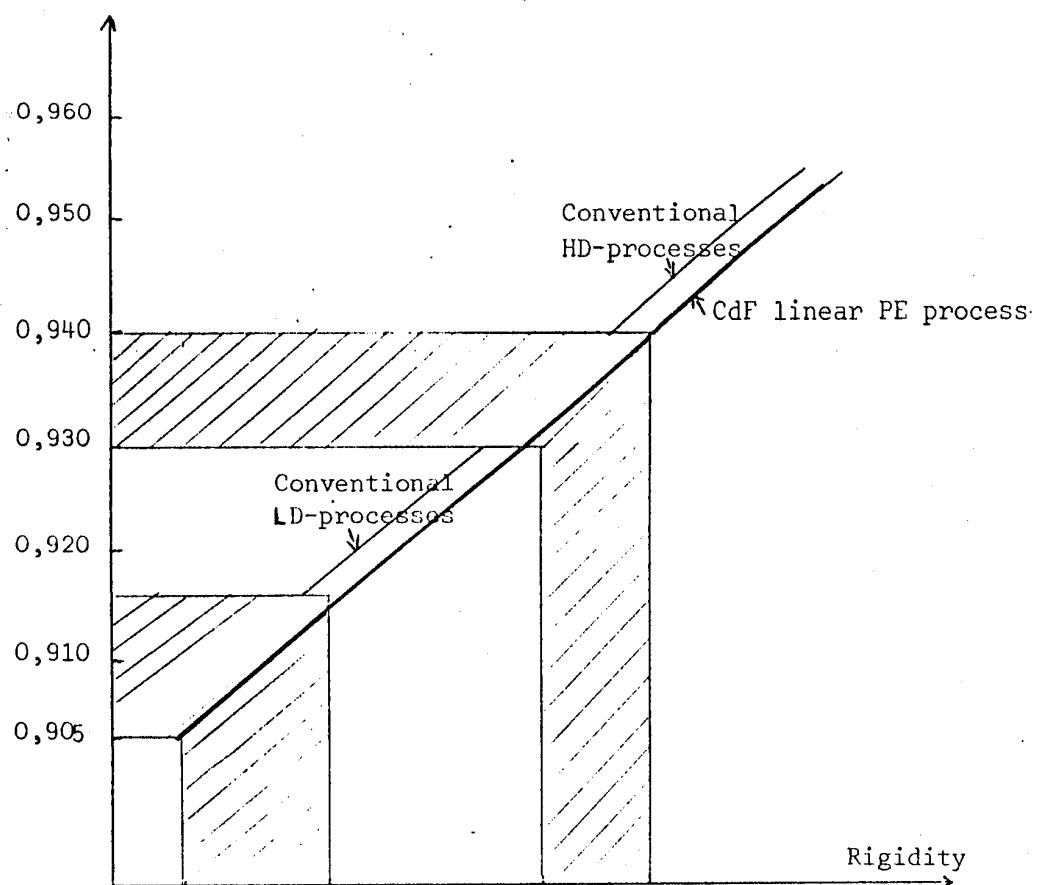
BASIS : Capacity : 2 MT ; Size : 140cm x 100 cm x 160 cm

	Cost break-up	PE film based bin with internal walls built of unburnt bricks	Concrete bin	Mild Steel bin (thickness of 5mm)
		Cost Rs.	Cost Rs.	Cost Rs.
1 Material cost	103	675		850
2 Cost for man hole and exit pipe		15-00	100	100
3 Fabrication cost		Negligible	50	250
4 Total cost		118-00	845	1200

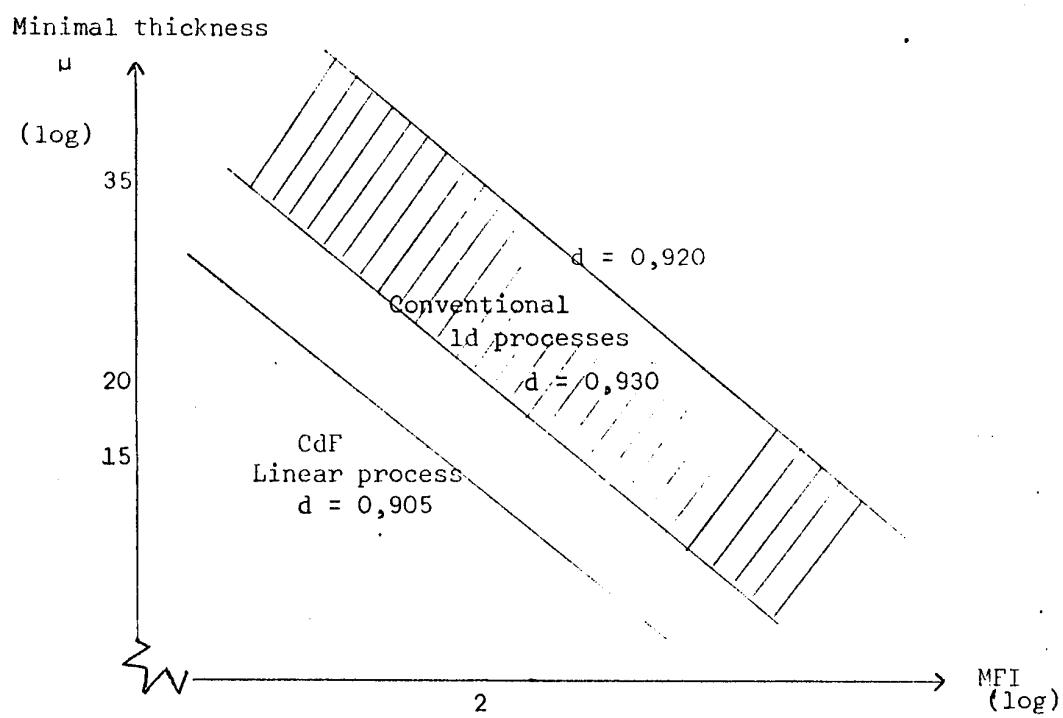


HIGH PRESSURE ZIEGLER PROCESS

The most important parts of the plant, usually encountered in high pressure low density polyethylene process, are maintained and process scheme is similar. There are some particularities however as far as monomer purifying, reactor and separators are concerned.



//: New applications opportunities



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HIGH DENSITY POLYETHYLENE

The purpose of this paper is to make understandable how HD-PE is made, how resins properties can be adjusted and what kind of resins are required for the main applications.

The descriptions cover only selected fields of the HD-PE industry and are focused mainly on particle form processes.

After a brief historical survey of the discovery of HD-PE processes, general principles of anionic coordinated catalysts are recalled. The means of achieving a given type of resin are discussed versus theoretical and practical considerations about the polymerization mechanism and kinetics.

The case of Ziegler processes is thoroughly considered. The evolution from classical processes involving a de-ashing step to modern processes using high activity catalysts and without a de-ashing step is discussed. The Phillips process is also analyzed and other newer processes are shortly presented.

The paper concludes with a discussion of important properties of HD-PE resins, the ways they can be adjusted and how to orientate the choice of a resin for a given application.

- - -

by André J. DELBOUILLE

(Solvay & Cie, Brussels)

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ENCLOSURES : - 5 figures
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I - INTRODUCTION

Whereas many high molecular weight polymers obtained, either by radical or ionic polymerization have been known for a long time, high molecular weight polyethylene was made for the first times by polymerization :

- In March 1933 by Fawcett-Gibson et al at ICI laboratories as far as radical polymerization of ethylene under high pressure is concerned.
- During World War II by Max Fischer at BASF laboratories as far as anionic polymerization of ethylene under low pressure is concerned.

Though the process discovered by Fischer involved the same catalytic species as the ones of Ziegler catalysts that we are going to describe, it was not developed industrially probably owing to an unacceptable polymer contamination by catalysts residues.

Another twenty years were necessary to have true low pressure polymerization processes.

The Ziegler process is the result of a systematic study by Karl Ziegler and his team at Max Planck Institut of the reaction of ethylene with alkylaluminums. Historically, the discovery of the so-called Ziegler catalysts was initiated by an abnormal experiment by Holzkamp in which only ethylene dimerization was observed due to, as was established, colloidal Nickel in the reactor.

The first systematic studies were then made by Breil and Martin who finally showed the high efficiency of Titanium based catalysts for ethylene polymerization. Many patents were filed from 1953 onwards. On his side, G. Natta started studying stereospecific propylene polymerization with Ziegler type catalysts and initiated the discovery of isotactic polypropylene processes which are described in patents starting in mid 1954.

Independently, J. Paul Hogan at Phillips Petroleum, during a study of gasoline synthesis starting from liquified petroleum gas, especially propylene and ethylene, discovered the principle of the so-called Phillips catalysts consisting of chromium oxides supported mainly on silica and silica-alumina and first patented in 1954.

Also at the same time, Seelig at Standard Oil of Indiana discovered and developed molybdenum oxide supported catalysts, active for ethylene polymerization, on which the so-called Standard Oil of Indiana process is based.

These early processes were not completely satisfactory of course and, as we shall see :

- the solution processes (Phillips and Standard Oil) were handicaped by high solvent usage and their catalyst removal step

- the Phillips suspension process suffered from a lack of flexibility for obtaining low molecular weight resins
- the Ziegler process implied the need for a sophisticated catalyst removal step.

Besides logical process improvements, it was obvious to try to develop high activity Ziegler type catalysts in order to suppress the de-ashing step.

This goal was achieved differently by several companies. Two main distinct approaches were followed :

- developing high activity complex catalysts, most of them involving magnesium compounds ; Hoechst, Mitsui, Montedison, Naphtachimie, Shell, Solvay and many others developed such catalysts
- developing highly active precipitated $TiCl_3$; Hoechst, Mitsubishi and several others studied and are probably using such catalysts.

From the process point of view, there was an evolution from solution processes to suspension and gas phase processes without forgetting high pressure processes using Ziegler catalysts.

Hereafter is presented a review of HD-PE questions. It is neither scientific nor exhaustive, its purpose is to give a comprehensive and didactic presentation of the various aspects and problems of the HD-PE industry.

II - GENERAL PRINCIPLES OF ANIONIC COORDINATED CATALYSTS

A - Foreword

For the present demonstration, we will only consider the case of Ziegler type catalysts. A similar picture could be given in the case of the other catalyst types.

B - Chemistry of Ziegler catalysts

In principle, Ziegler type catalysts are prepared starting with transition metal compounds of groups IVa to VIa together with organometallic compounds of groups I to III (and IV). The most important family is the one based on Titanium halides ($TiCl_4$, $TiCl_3$, $TiCl_x(OR)_{4-x}$...) and $AlR_x(3-x)$.

Figure 1 gives a sequence of likely reactions leading to active site formation in the case of the $TiCl_4 - Al(C_2H_5)_2Cl_x(3-x)$ system. Both homogeneous and heterogeneous Ziegler catalysts are known.

C - Polymerization mechanism

Our purpose is not to review this matter or the polymerization kinetics. However, we would like to justify the practical rules of polymerization control by some fundamental considerations.

As far as the polymerization mechanism is concerned, we refer to the Cossee explanations which are the most used in the literature for Ziegler catalysts and which can be adapted to other catalytic systems.

According to Cossee, the active site is constituted by a transition metal atom in an octahedral environment in which there is at least one coordination vacancy corresponding to a missing ligand.

$X_1 \dots X_4$ are the anions in the crystal lattice (Figure 2). Their nature, their number and their location determine in principle the behaviour of the catalyst which has to be considered as containing several kinds of active sites in proportions which vary from one catalyst to another.

Polymerization works according to the chain mechanism described in the same figure 2.

Three steps are distinguished :

- olefin complexation in the anionic vacancy
- induced polarization of the olefin double bound
- insertion of the olefin molecule.

D - Polymerization kinetics

The various main steps that are identified in olefin polymerization are shown in figure 3.

Olefin polymerization is generally first order with respect to monomer.

Figure 4 shows the polymerization degree D_p theoretically given by the relationship based on figure 3 and in which (S) is the active site concentration and neglecting the initiation step.

According to these simple equations, the polymerization degree or better the molecular weight can be adjusted by :

- varying the polymerization temperature
- introducing hydrogen in the system ; this is the most commonly used technique
- adjusting monomer, comonomer and activator concentration.

It should be understood that the k values in these equations refer only to one type of active site.

Practical catalysts comprise in various proportions several types of active sites whose k's are different.

The different behaviour of the very many different industrial catalysts can be explained in this way.

III - CHARACTERISTICS OF THE MAIN LOW PRESSURE PROCESSES FOR ETHYLENE POLYMERIZATION

A - Ziegler processes

1 - Introduction

Two types of classical processes are known :

- suspension or particle form process : this process involves an inert diluent (isobutane, pentane, hexane, heptane, naphta, petroleum cut) and one heterogeneous catalyst, most often based on titanium compounds and alkylaluminums ; a technological limit of this process is the bulk density of the flake which determines the reactor output
- solution process implying an inert diluent at various temperatures and using both heterogeneous and homogeneous catalysts ; a technological limit of this process is the viscosity of the solution which is influenced by polymer concentration and polymer molecular weight ; we will not consider this type of process in our discussion.

2 - Classical processes

Classical Ziegler catalysts are not very productive and give polymers which are contaminated by catalyst residues, mainly Ti, Cl, Al which must be eliminated to obtain thermally and photochemically stable as well as non corrosive polymers. These desired properties of the end product are obtained by post-treatments of the polymer suspension or by adequate additives.

Most generally, catalyst residues are removed by dissolving them in anhydrous polar organic compounds (alcohols...) neat or mixed with the polymerization diluent.

Flow sheets of such classical Ziegler processes are generally characterized by :

- flashing and removal of the gaseous effluent
- centrifuging the polymer suspension and removing the diluent and the soluble, low MW polymer fraction
- alcohol treatment of the polymer
- washing by various techniques the treated polymer with clean diluent and separation of the diluent-alcohol mixture loaded with catalyst residues
- centrifuging the polymer
- water stripping the purified polymer suspension
- centrifuging the water
- drying the polymer

The complexity of such a process lies also in the diluent recovery section where one must avoid contacting simultaneously diluent, alcohol and water due to ternary azeotrope formation which would disturb the system.

Several operations must be carried out :

- wet diluent drying
- alcohol removal from the diluent
- low polymer elimination

Moreover, the alcohol-diluent mixture must be carefully dried before being introduced again into the polymer purification unit.

To summarize, this type of process requires careful control. Raw materials and energy usage are on the high side.

3 - Improved processes

The use of superactive catalysts dramatically simplifies the manufacture flow sheet. Figure 5 presents as an example the flow sheet of the Solvay process. To be pointed out :

- direct water stripping of the polymer suspension
- centrifuging the water
- drying the polymer in a fluid bed dryer.

B - Phillips process

Phillips catalysts operate according to a mechanism similar to the Ziegler catalyst one but here, the main means of molecular weight control is not hydrogen but polymerization temperature : the higher the temperature, the lower the molecular weight.

This peculiarity forced the development of a solution process operating above the dissolution temperature of HD-PE in the considered diluent : Phillips SF solution form process.

The catalyst based on chromium oxide supported on various types of silica and silica-alumina is eliminated by centrifuging and filtering the polymer solution. Technological and economical performances of such a process are limited by the viscosity of polymer solutions though special types of reactor were developed. That is why this process is being progressively abandoned.

However, Phillips concentrated their research efforts on a suspension process operating in a light hydrocarbon (isobutane, pentane...) at a temperature below polymer dissolution : Phillips PF (particle form) and PPF (processable particle form) processes. Difficulties with these processes, very interesting from a technological and economical point of view were the developement of catalysts flexible enough to lead to sufficiently low molecular weight polymers under conditions imposed by a suspension process. No polymer purification is necessary owing to the high activity of the catalysts in the PF process.

This limited flexibility in the polymerization section was compensated for by the development of a blending technology of SF, PF and PPF flakes in order to satisfy the different blow molding and extrusion applications. Injection application required either SF resins or depolymerized PF resins.

C - Standard Oil of Indiana process

As already mentioned, this process involves a molybdenum oxide supported catalyst whose productivity is said not to be very high. This determines a solution process in which the catalyst must be removed. This process is not very well known from the literature and is not very developed. That is why it will not be discussed further.

D - Gas phase processes

Several gas phase processes are known e.g. :

- fluid bed processes : Union Carbide, Naphtachimie...
- stirred bed processes : BASF, Amoco...

The development of such gas phase processes implies developing new catalysts or new catalyst properties such as particle size, abrasion resistance, etc... The economics of these processes are an important and interesting development. We will not go into further details.

E - Miscellaneous

Besides the processes mentioned above, a few companies have developed bulk high pressure processes e.g. : ABCD SNAM Progetti, Sumitomo, CDF-Chimie... It is beyond the scope of this lecture to review such processes in detail.

IV - FINISHING OF HD-PE RESINS

At the dryer outlet, the HD-PE powder usually has to be pelletized with stabilizers and additives in order to obtain the commercial resins or compounds.

Pelletizing can be omitted in some cases and then the powder must be homogenized and stabilized to make "premix". Both pellets and premix are sold in bags, in containers or by truckload.

V - CONTROL OF POLYMER PROPERTIES

It is compulsory for modern processes to be flexible and able to satisfy a range of applications for which it is not rare to make tailor-made resins.

The flexibility of a process is the ability to control directly in the reactor the main properties of the resin i.e.

- Molecular weight, currently measured by the melt index at 190 °C (MI).
- Molecular weight distribution (MWD) measured either by Gel Permeation chromatography (GPC) or by rheological determinations on molten polymer (shear sensitivity).

- Density reflecting short-chain branching (SCB) and linked to crystallinity, stiffness, brittleness and stress-cracking resistance (ESCR).
- Long-chain branching (LCB) estimated by a combination of physico-chemical measurements can also affect the above properties.

The influence of these primary parameters are noticed e.g. on injected part warpage, rheological properties of blow molding resins mainly, stretchability, stress-cracking resistance.

These four fundamental properties can be controlled by acting on :

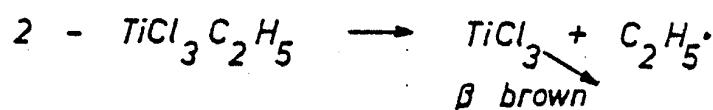
- type of catalyst and its recipe to adjust MWD
- hydrogen concentration to adjust MI
- comonomer type and concentration to adjust density and ESCR
- polymerization conditions for fine tuning.

Table 6 indicates the influence of the main parameters on resin processability and finished part properties.

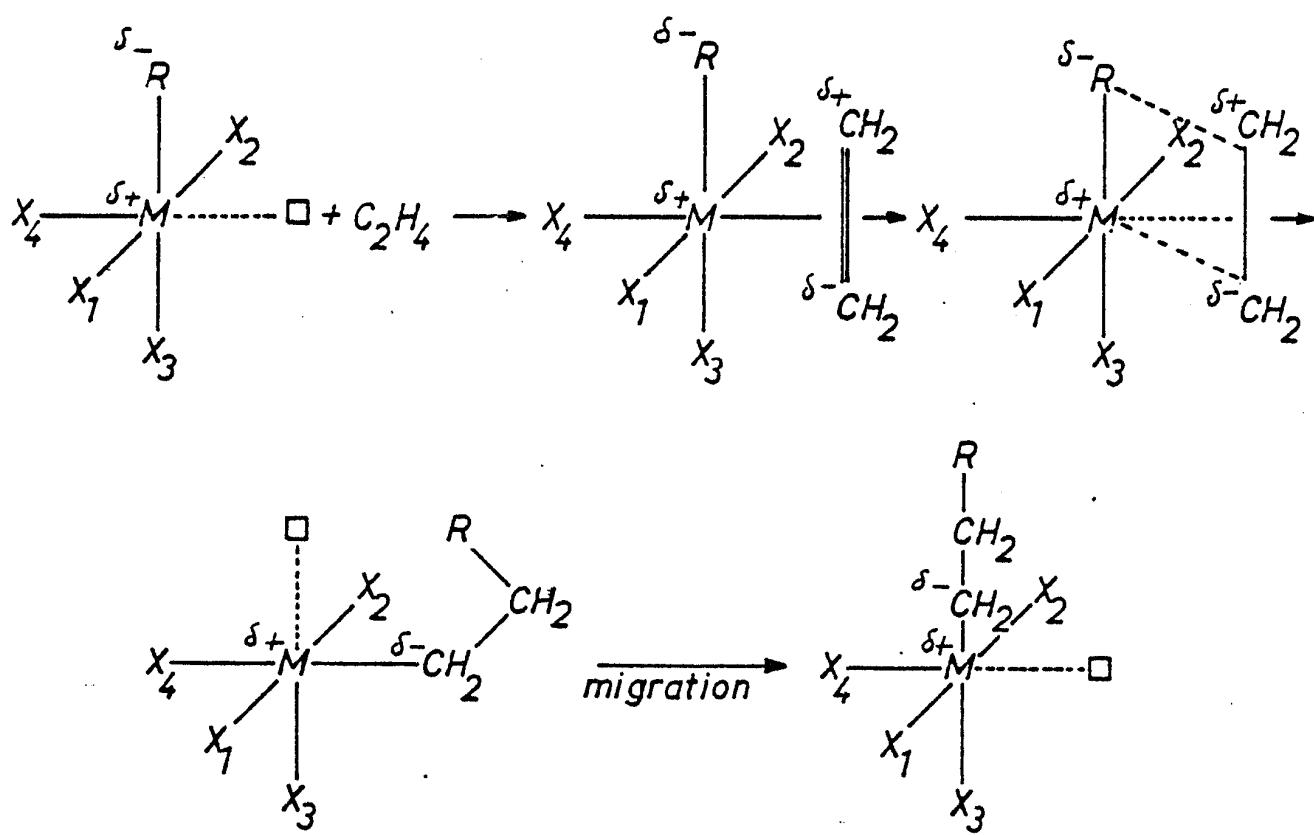
ENCLOSURES : - 5 figures
- 1 table

Figure 1

Example of active site formation in Ziegler-Natta catalysts



Ziegler-Natta catalytic site (according to Cossee)



M : transition metal ion

R : alkyl or growing polymer chain

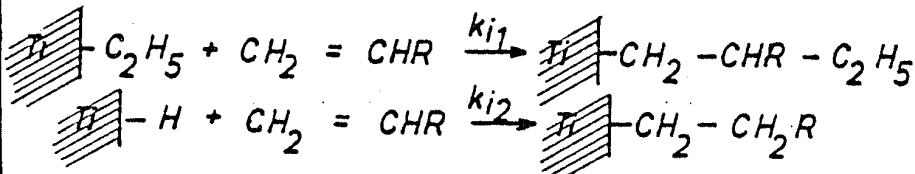
$X_1 \dots X_4$: anion

$\square \dots$: anionic vacancy

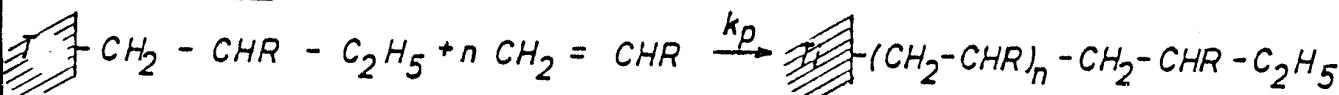
Figure 3

Kinetic scheme of olefin polymerization

1 - Initiation

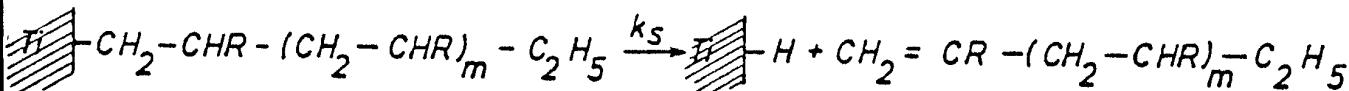


2 - Propagation

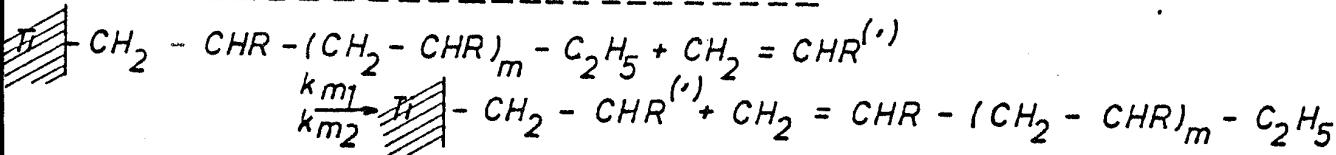


3 - Transfer

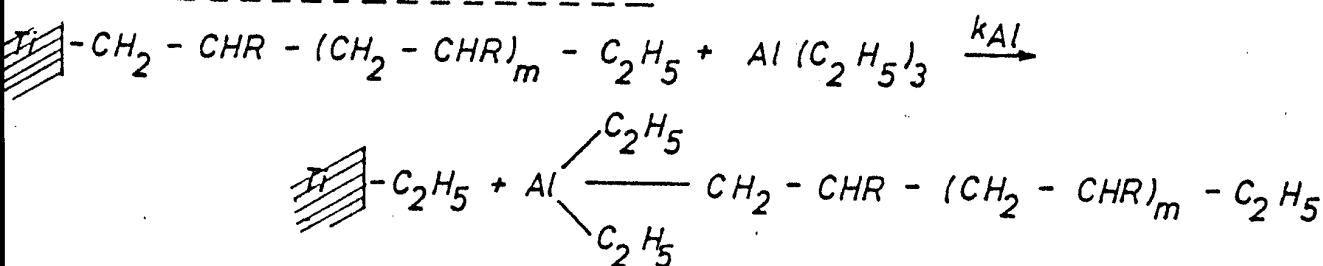
a - spontaneous



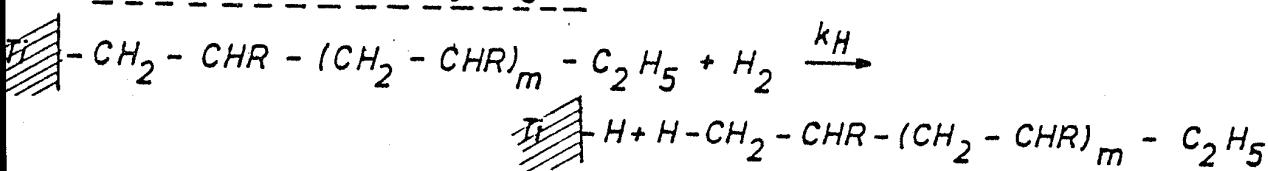
b - under the action of monomer or comonomer



c - under the action of the activator



d - under the action of hydrogen



- Termination

By reaction of active sites with impurities, by spontaneous decomposition of this one or often by coating of catalyst particles with the polymer

Figure 4

Polymerization kinetics of ethylene in the case of
Ziegler-Natta catalyzed processes

$$D_p = \frac{\overline{M_n}}{28} = \frac{\text{propagation rate}}{\text{Sum of termination + transfer rates}}$$

$$= \frac{k_p [S][M_1]}{k_s [S] + k_{m1} [S][M_1] + k_{m2} [S][M_2] + k_{Al} [S][Al] + k_H [S][H_2] + k_D [S][P]}$$
$$= \frac{k_p [M_1]}{k_s + k_{m1} [M_1] + k_{m2} [M_2] + k_{Al} [Al] + k_H [H_2] + k_D [P]}$$

where

[S] = active sites concentration

[M₁] = main monomer (ethylene) concentration

[M₂] = comonomer concentration

[Al] = activator concentration

[H₂] = hydrogen concentration

[P] = poisons concentration

k_p : propagation constant

k_s : self termination constant

k_{m1} : transfer constant with main monomer

k_{m2} : transfer constant with comonomer

k_{Al} : transfer constant with the activator

k_H : transfer constant with hydrogen

k_D : termination constant with poisons

Flow scheme of the Solvay HDPE process

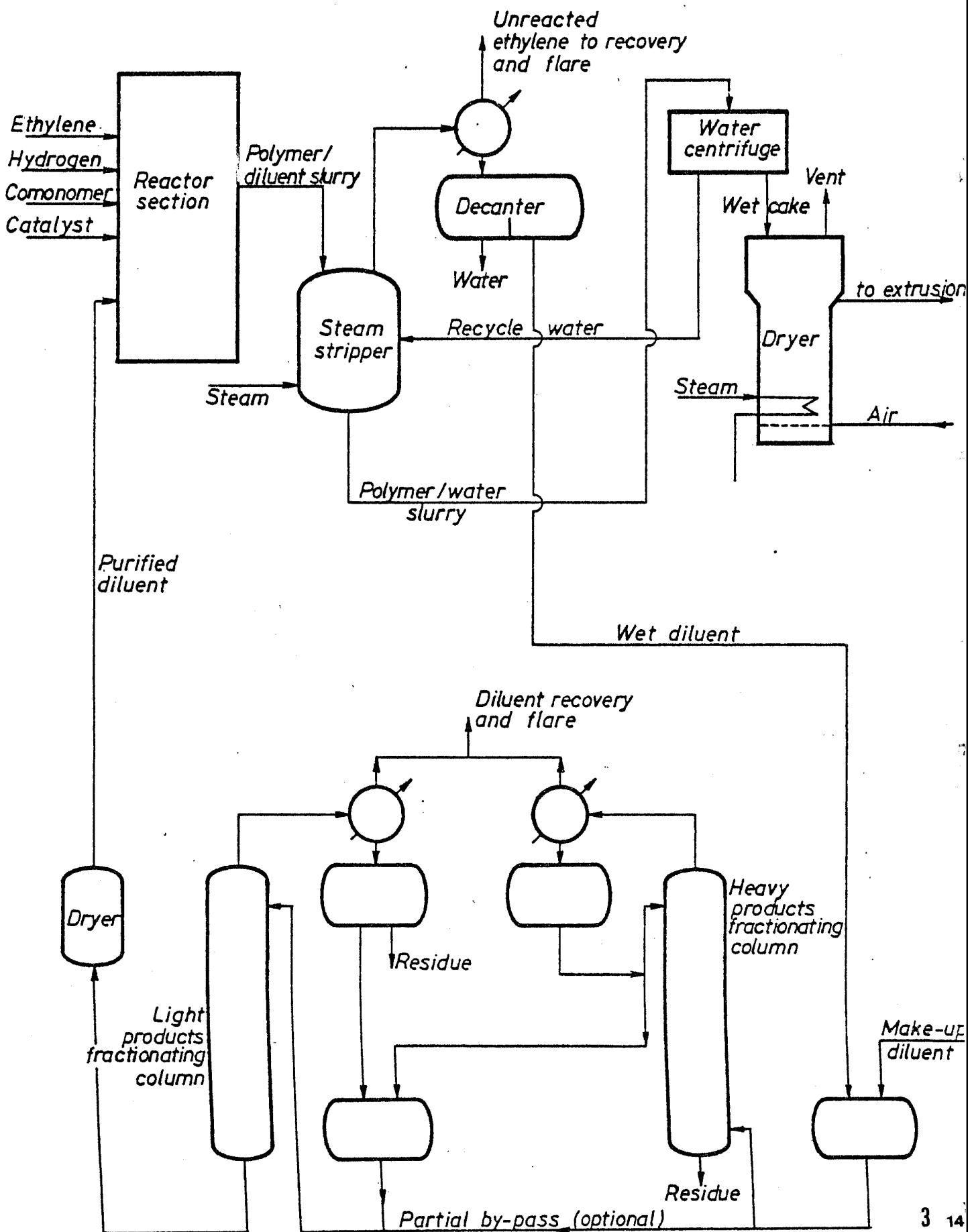


Table 6

Influence of molecular weight distribution (MWD) density (D)
and melt index (MI) on processing characteristics of Eltex
resins and on properties of finished products.

Legend:

↗ = increase

↘ = decrease

○ = no effect

✗ = some influence, but this depends on
 the method of processing or on the
 type of the application.

1. Behaviour during processing	Desired tendency	Requirement		
		MWD	D	MI
Injectability	↗	broad	○	↗
Prevention of warping	↗	narrow	○	↗
Extrusion rate	↗	broad	○	↗
Reduction of swelling	↗	narrow	○	±○
Resistance to elongation in the molten state	↗	broad	○	↘
Prevention of sharkskin	↗	broad	○	↗
2. Mechanical characteristics of the finished objects				
Stiffness	↗	○	↗	○
Environmental stress cracking resistance (ESCR)	↗	✗	↘	↘
Impact strength	↗	narrow	↘	↘
Creep resistance	↗	✗	↗	↘

POLYOLEFINS - RECENT IMPROVEMENTS

POLYPROPYLENE

G Campbell
ICI Plastics Division
England

ABSTRACT

Business opportunities for polypropylene are being continually expanded by improvements in polymer properties, stabilisation and modification by fillers and reinforcing agents. Significant developments also are taking place in conversion technology.

Brief reference is made to new polymerisation processes but these are not discussed in depth as the main objective is to show how technological advances are leading to new performances and hence to new applications.

Polypropylene, still the newest of the large tonnage production thermoplastics, has in fact achieved its "commercial majority" at the age of 21. Whereas most humans at this stage in life span may be regarded as fully developed physically, polypropylene continues to grow and to develop new features and versatility.

Versatility is indeed the key word to describe polypropylene and this versatility is being extended by development of base resins and of blends, filled and reinforced variants of improved performance in toughness, flexural modulus and deformation temperature. As has been said frequently over past years, it is possible to look at each individual property of polypropylene and to find that property excelled by the same individual property of another polymer. What few, if any other polymers can do is to better polypropylene in a combination of properties and an ease of processing which suit it to the end-use requirements and conversion processes of so many industries.

A polymer which can provide bumpers for automobiles and house their heating and ventilating systems, which is used for carpet backings and face fibre, for packaging films for foodstuffs and cigarettes, for moulded margarine tubs and bottle and produce transportation crates, for pipes for under floor heating and for chemical plant and for sterilisable hospital wares - just to name a few uses - cannot be described other than as versatile.

Major development areas for polypropylene are those already briefly mentioned

to improve the toughness/stiffness balance of base resins

to develop new levels of toughness by blends

to develop new levels of stiffness and higher deflection temperatures by filling and reinforcement.

Ideally one would wish to be able to improve all these factors in one and the same product but this is not an ideal world and some compromises have to be accepted by the convertor and end user. Compromises are not necessarily wholly disadvantageous, however, and reference will be made to relationships between properties and how they influence end uses.

BASE RESINS

It is no longer possible, if it were ever so, to predict the properties of a homopolymer from knowledge of its solubles content and mean molecular weight or those of a block copolymer by adding information on its comonomer content.

New and improved catalysts are changing the balances of properties. High stereospecificity/stereoregularity is obtained by reduction in both the amount of atactic and the number of imperfections in the isotactic chains. Faster crystallisation rates and improved balances of properties result. Property improvements usually are utilised as 10 - 20% higher flexural moduli whilst retaining the same toughness as standard grades. An alternative approach is by leaving moduli unchanged but improving toughness, especially at low temperatures.

Reduced main chain stereoregularity, ie increased frequency of imperfections, also is an interesting development offering reduced stress whitening and somewhat improved toughness.

For many years little technological interest was shown in molecular weight distribution as a factor in the determination of properties and processing behaviour. Some early polymers were given higher melt flow rates by thermal degradation or vis-breaking but it is only recently that the narrowing of molecular weight distribution which frequently resulted has been recognised as having good practical advantages. Narrow molecular weight distribution is now usually obtained by other means such as densification of powders in the presence of peroxides which is a more controllable process.

These narrow molecular weight distribution (NMWD) polymers are used increasingly for spinning of fine fibres and for high output injection moulding of thin walled containers as they have good thermal stability and relatively low sensitivity to shear and thermal history. For fibres they provide higher line speeds and offer one route to higher tenacity. For injection moulding they offer reduced moulded-in strain coupled with somewhat improved toughness; melt flow index for thin wall mouldings now frequently exceeds 20 ($230^{\circ}\text{C}/2.16 \text{ kg}$) and 30 - 35 is not unknown although perhaps not yet common.

Significantly wider than normal molecular weight distribution polymers are unlikely to be of true interest as their melt viscosity is very sensitive to processing history through the very large molecules present at the upper end of the distribution.

Although the preceding remarks have been related mainly to homopolymers parallel developments are taking place in block copolymers. Block copolymers were introduced commercially in 1962 in order to obtain improved low temperature shock resistance by means other than blending with rubbers; the then available rubbers caused problems of phase separation, colour control and cost of incorporation but events often move in a full circle and blending with rubbers is now again a lively topic although with targets rather more ambitious than in the late 1950's and early 1960's; these newer aspects of blending with rubbers will be discussed later.

The more recently introduced block copolymers, obtained by catalyst and process modifications are aimed at two targets - higher moduli without loss of toughness and higher toughness without reduction in moduli - which will further extend uses. The significance of block copolymers in the UK is notable. It is estimated that they take about 75% of all injection moulding outlets which form 40 - 45% of the total market and about 45% of all polypropylene usage.

VERY HIGH IMPACT RESISTANT TYPES

Polypropylene is finding promising new outlets where very high impact resistance together with good resilience, moderate stiffness and deflection temperature are required. The most significant use at present is in car bumpers but there are lesser established uses as in steering wheel covering and prospects for fascias, parcel shelves and seat backs in cars.

These materials differ so greatly from traditional grades that they are now commonly classed as thermoplastic elastomers (OTE'S TOE and other terms are used).

Some typical properties and a typical car bumper installation are illustrated, the latter design to meet the US Federal impact test at 8 kph.

The preferred route to obtaining these very high impact strengths at present is by blending homopolymers or block copolymers with EPDM although EPR is perhaps equally suitable.

Further modifications of these materials to further improve certain properties is increasingly foreseen - incorporation of glass beads to improve scratch resistance, incorporation of particulate inorganic fillers to give greater stiffness and incorporation of mixed fibrous and particulate fillers to give greater strength and stiffness.

This work is as yet aimed primarily at the automotive industry but these products have potential also for other industries requiring high shock resistance, resilience and high deflection temperatures.

As in all life some compromise has however to be accepted. If increased scratch resistance or increased stiffness is obtained by incorporation of inorganic fillers there is some loss of

impact resistance resulting from the discontinuities caused by filling. The user has still to decide upon that property which is most important to his requirements but the number of composition variables is so great that such a compromise is unlikely to prove unduly troublesome.

FILLED AND REINFORCED COMPOSITIONS

Something has already been said on this topic with reference to very high impact grades. There are, however, at present more numerous requirements for additional stiffnesses and higher deflection temperatures than for very high impact types - although if the OTE bumper is fully proven in service the pattern may well change in the future.

A word of caution on the cost consequences of filling appears appropriate. The low specific gravity of polypropylene lies at the root of the problem as the cheaper fillers have densities about three times that of the polymer with which they are blended. Commonly used particulate fillers such as talc, chalk/limestone, glass microspheres increase the density of the blends significantly and thereby reduce the volume per tonne of raw material, and although the fillers may be in themselves cheap, there are additional costs of compounding and in some cases additional stabilisers are needed as fillers can deactivate standard stabiliser systems and cause premature oxidative breakdown. All coins have, however, two sides and the use of fillers frequently permits moulding of thinner sections with less volume use of material and faster cycling speeds through reduced cooling times in injection moulding.

The first two fillers to achieve prominence in polypropylene were asbestos and glass fibres. The former held for several years a dominant position in the automobile industry for fan shrouds and heater casings but has now been withdrawn by most manufacturers as likely health hazards from asbestos have increasingly been recognised. For many uses talc replaced asbestos but it in turn has increasingly been replaced by chalk or limestone. Limestone (or chalk) does not increase flexural modulus to the same extent as does talc but, perhaps surprisingly, it slightly improves rather than reduces the impact resistance of homopolymers; unfortunately the same effect is not observed with copolymers.

Talc and chalk/limestone filled polypropylenes have major uses in injection mouldings for the motor industry and some interest has been generated in limestone filled polypropylene as a substrate for fabric finished internal trim for cars. For such trim, fabric is laminated directly to the filled polypropylene sheet as the latter is extruded and the resultant laminate can be thermoformed to yield trim panels with greater styling freedom than is practicable with the more traditional hardboard substrates. These polypropylene/fabric laminates will compete in some trim work with injection moulded components to which melded fabrics are laminated during the injection process; a recently introduced variant is the use of polypropylene coated fabric which can be partially thermoformed as the injection mould closes and is subsequently "backed" by polypropylene during the injection stroke; this enables a wider range of fabrics to be used.

Of the other particulate fillers wood-flour perhaps currently presents greatest interest because of its low density, ready availability and low cost. Wood flour/polypropylene compositions are not really new - patents date back to about 1960 - but were - of limited interest until the demands for car weight reduction started to bite hard as the high moisture content and readiness to charring of wood presented production problems. Wood flour filled polypropylene is an alternative to mineral filled polypropylene for the extruded/thermoformed panels just discussed. There is suspicion in some quarters about their toughness and hence suitability for car interior trim but it would be unwise to assume that this problem - if it does exist - is incapable of resolution.

Limited work has been done over many years with mica as a filler for polypropylene but there is little evidence yet of significant commercialisation. Early work with mica, which is platelet in form rather than particulate, showed a tendency to yield weak welds in mouldings and it is by no means certain that this problem has been fully resolved.

Glass beads and microspheres also are used, mainly to obtain additional hardness and to reduce the anisotropic shrinkage which occurs with glass fibres.

Glass fibre, one of the most important fillers, has been left intentionally to the end of this resume of filled compositions as glass fibre can be used as both a filler and a reinforcing agent and thereby leads directly to a discussion of reinforcement as opposed to simple filling.

With a majority of filled compositions there is no bonding of the filler to the polypropylene. The situation differs from that met with polyamides where hydrogen bonding takes place between glass fibres and the base resin. With polypropylene, it is necessary to use a chemical bonding agent to obtain adhesion between glass fibres (or other reinforcements) and polypropylene. To put matters simply, perhaps too simply, if one has a simple filling of polypropylene, the tensile properties as temperature rises decay rapidly as the strength is only that of the 60, 70, 80 or other percentage of the composite which is polypropylene. With the coupling agent present, one has the tensile properties of the glass fibres added to those of the polypropylene and hence a range of materials of much superior properties over almost the entire service temperature range. Slides compare the structures at break of simple filled and of reinforced glass fibre compositions as shown by scanning electron microscopy.

Although chemical coupling is presently applied almost exclusively with glass fibres there are no real reasons why it should not be applied equally to particulate fillers - although the geometry of particulates is likely to limit to some degree the improvements obtainable.

This has been indeed only a resume of the present and likely future development of filled and reinforced polypropylene. With increasing energy requirements and possible decreasing feedstock availability for all plastics materials, filling and reinforcement will play an increasing future role.

STRUCTURAL FOAMS

Polypropylene is one of the most rapidly developing materials for structural foams. It is not intended here to discuss structural foams as such - the process alternatives are already widely known. What is perhaps of most significance for the future is the use of filled and/or reinforced structural foams.

To speak of a filled structural foam may sound an absurdity but such materials incorporating hollow silicate microspheres have been in successful use for several years now in rudders and dagger boards of sailing dinghies and for brush handles. Of more recent development and likely great future significance is the development of glass fibre reinforced structural foams for quite major engineering components such as the outer drums of clothes washing machines. For that example shown the alternative materials were vitreous enamelled steel, stainless steel or aluminium which would have required 16 individual parts, welding operations and possibly subsequent anticorrosion coating - as opposed to a single shot injection moulding. Glass fibre reinforced structural foam can truly be classed as a significant new material amongst the so-called engineering polymers.

CONCLUSIONS

Of necessity this has been an incomplete, time limited review of what has been happening in recent developments with polypropylene. Before closing, however, it is necessary to note the advances in light stabilisation resulting from the introduction of new systems such as the hindered amines; of the progress made in introducing

dyeable and printable polypropylenes for carpets and upholstery fabrics; of improved electroplating systems. The list is extensive and in the author's view fully supports the earlier expressed view that although polypropylene has achieved its majority in numbers of years, it has by no means yet achieved its full development.

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SOME ASPECTS OF ORIENTATED POLYPROPYLENE

IN FILM, THERMOFORMING AND BOTTLE APPLICATIONS

by

Dieter H. BUERKLE

and

Jean-Claude MOULIES

Polypropylene Product Development
ATO CHIMIE, Usine de MONT
F-64300 ORTHEZ, France

CERDATO
ATO CHIMIE
F-27470 SERQUIGNY, France

ABSTRACT

The development of improved polypropylene resins with a better compromise between low temperature sealability and good optical and slip properties opens new markets for biaxially orientated polypropylene packaging films. In the capacitor film area, extremely pure resins have been developed for the production of very thin biaxially orientated polypropylene films.

Depending on forming conditions, a certain degree of orientation can be imparted to thermoformed items. In addition, specially designed Ethylene/Propylene random copolymers yield better optical and impact properties.

Stretch blowing of polypropylene is a quite new field but should become an expanding market in the next few years, provided that machines with a lower capital cost/output ratio will become available.

INTRODUCTION

During the last few years, polypropylene has become the commodity plastic with the highest expansion rate with an expected increase of 10 to 15% during the next few years in Western Europe.

This optimistic picture stems from several facts. Firstly, polypropylene, the youngest big volume plastic, has just come of age. Secondly, its low price, together with outstanding properties, open a very wide market. And finally, most basic characteristics of polypropylene are highly influenced both by the resin production process and extrusion conditions and thus make polypropylene an extremely versatile plastic.

Development of improved polypropylene grades, together with adapted converting systems for bi-axial orientation, gives polypropylene the possibility to penetrate new markets.

ORIENTATED POLYPROPYLENE PACKAGING FILMS WITH LOW HEAT SEAL TEMPERATURE

Biaxially orientated polypropylene film has already been a serious contender for cellophane replacement for several years. Whilst cellophane films need an expensive lacquer coating to give them good heat seal properties at low sealing temperatures, co-extrusion of polypropylene and a thin layer (1 μ or less after orientation) of resin with relatively low melt temperature is more economic. For this sealing layer, the best compromise had to be found between relatively low heat seal temperature, excellent optical, slip and antistatic properties for use on high speed packaging machines.

Ethylene/propylene random copolymers are already widely used for the heat seal layer, because of their lower melt temperature which gives the possibility of sealing the multi-layer film without the central polypropylene homopolymer layer loosing its orientation. Fig. 1 shows the melt temperature (upper curve) and the minimum sealing temperature (lower curve) of E/P random copolymers as a function of ethylene content. In the particular case of fig. 1, unstretched water-cooled film samples were sealed. The minimum sealing temperature was defined as the temperature giving a minimum of 300 g/15 mm seal strength (at normal sealing pressure).

For orientated films, the minimum sealing temperature tends to be slightly higher (see table I).

Ethylene content in E/P random copolymers	Minimum sealing temperature at	
	normal sealing pressure	low sealing pressure
3.4 %	130° C	133° C
4.2 %	120° C	126° C

TABLE 1 : Minimum sealing temperature for different E/P random copolymers after co-extrusion with polypropylene homopolymer and subsequent stretching.

Co-extruded flat OPP-film systems are available for up to 8 m film width (after transverse stretching). One of the latest developments in this field is a co-extrusion die, which prevents the copolymer sealing layer from spreading over the whole width to the edge. It became therefore possible to obtain a nearly copolymer-free edge-trim which can be fed back in the main extruder without reducing the stiffness of the central homopolymer layer.

OPP CAPACITOR FILMS WITH IMPROVED ELECTRICAL PROPERTIES (1)

Biaxially orientated polypropylene films have made a big inroad in miniature condensors for the electronics industry. Film thicknesses (after orientation) of 6 microns, and less, are already commercially available.

Two conditions were necessary to obtain these very thin films with outstanding electrical and ageing properties : firstly extensive work on the improvement of flat film tenter lines such as modified clamp design ; and secondly the development of very pure highly crystalline polypropylene resins with excellent stretching and electrical behaviour. Fig. 2 shows the influence of the isotacticity index (heptane insolubles) on the dielectric loss of polypropylene homopolymers. The isotacticity index gives approximatively the amount of stereoregular isotactic chains opposed to irregular, non crystalline atactic chains (2).

The influence of traces of catalyst residues on dielectric loss of polypropylene homopolymers is shown in fig. 3 (2).

It is obvious that only polypropylene resins, produced by a process giving extremely low catalyst residues and high isotacticity, will yield low dielectric losses.

ORIENTATION IN THERMOFORMED POLYPROPYLENE CONTAINERS

Considerable work has been done on thermoforming of polypropylene at relatively low temperatures, eg. (3). It has been shown (4) that it is not possible to thermoform unfilled polypropylene at temperatures above the final melting point.

Consequently, a certain amount of orientation is imparted to polypropylene during thermoforming. One of the main factors is the sheet temperature during the forming step. Fig. 4 clearly shows the increased orientation at lower forming temperatures leading to increased yield strength. Transparency (fig. 5) and surface gloss also increase markedly with decreasing forming temperature for all types of polypropylene (4).

Especially with E/P random copolymers outstanding transparency and surface gloss can be obtained (fig. 6). On the other hand, high orientation at low forming temperatures brings along relatively high shrinkage (fig. 7).

The bottoms of thermoformed polypropylene containers are slightly biaxially orientated. Fig. 8 shows the increase of impact resistance of the bottom of tubs with decreasing forming temperature. The test device used was ATO CHIMIE's "ECLATOMETRE" where a hydraulic shock is applied to the sample. The volume of liquid displaced at failure is an indication of the shock resistance.

Bearing in mind some outstanding properties of polypropylene such as heat resistance up to 120° C and higher, excellent stress crack and grease resistance and low density (0.905 g/cm^3), its market volume in the sheet and thermoforming area seems still surprisingly low. In the past, this was mainly linked to difficulties in thermoforming conventional homo- and block copolymers because of their sharp melting point which gave a relatively narrow temperature range for thermoforming (fig. 5). These difficulties made machine manufacturers modify their equipment on the sheet extrusion and, more especially, on the thermoforming side, by developing special machines for polypropylene. The key point is, in all cases, precise temperature control.

In addition, the availability of E/P random copolymers, with a relatively wide forming range may give a new impetus to polypropylene in the sheet and thermoforming area.

STRETCH BLOWN POLYPROPYLENE BOTTLES

The unstretched polypropylene bottle market has become a fast growing sector over a short period of time, especially for detergent, food and pharmaceutical packaging. In nearly all cases, conventional HDPE equipment, but with polished molds, is used today.

.../

5 3

E/P random copolymers are already frequently used. The random copolymerisation with ethylene yields a decrease of crystallinity (fig. 9) measured by Differential Scanning Calorimetry (DSC) (*). In addition, the average spherulite size, measured by LASER light diffusion pattern, decreases with increasing random ethylene content (fig. 10).

Both decreasing crystallinity and average spherulite size give significantly improved melt strength, transparency, surface gloss and cold impact resistance. On the other hand, stiffness is slightly reduced with increasing ethylene content. The right balance between these properties leads to very attractive and price competitive containers (fig. 11).

With the exception of sterile solution packaging for pharmaceutical applications, the use of stretch-blown polypropylene bottles is rather new.

Only few machines for the production of OPP bottles are available now. In all cases, the extruded or injection molded preforms are cooled down to room temperature, reheated to nearly the melting point, then stretched lengthwise and afterwards in the transverse direction by blowing.

Fig. 12 shows clearly that a significant improvement of optical properties can be obtained by stretch blowing polypropylene bottles. Surface gloss and transparency of stretch blown random copolymer bottles are comparable to those normally obtained only with amorphous polymers (fig. 12, right side).

In addition, with orientation bottle weight can be reduced significantly. Table 2 shows the increase of maximum top load and drop impact resistance with orientation.

	Polypropylene homopolymer		Ethylene/propylene random copolymer	
	Conventional	Stretch blown	Conventional	Stretch blown
Bottle weight (g)	23	21.5	23	21.5
Max. top load (N)	265	315	150	235
Drop impact resistance (50% fail) at 0°C (m)	Less than 0.50	Less than 3.50 (1)	2.25	More than 3.50 (2)

(1) Only 30 % fail at 3.50 m.

(2) Only 4 % fail at 3.50 m.

TABLE 2 : Influence of orientation on bottle properties. Stretch blown bottles were blown from injection moulded preforms. Stretch ratios : lengthwise 1.85 : 1, radial 3.1 : 1.

(*) The heat of fusion for a 100 % crystalline polypropylene was taken as 45 cal/g.

Two major factors have prevented a wider use of the stretch blowing technology in the case of polypropylene in spite of the cited advantages.

The first one is that no polypropylene equipment with in-line parison formation and subsequent blowing is in commercial use, because of the relatively low freezing temperature of polypropylene (5). Work is under way at resin producers with polypropylene having increased freezing temperature by adding nucleating agents and at machine manufacturers with new in-line systems.

The second reason for the slow move of polypropylene in the OPP bottle field is the need for very precise temperature control with polypropylene homopolymers. Fig. 13 shows that compared to the extremely narrow stretch temperature range of polypropylene homopolymers (2° C) random copolymers can offer a more viable range of 10° C and more.

It can be expected that in the next few years stretch blowing of polypropylene bottles will become an expanding market, although much work has still to be done on machine and resin development.

CONCLUSIONS

Orientation has been shown to be an interesting converting step for a number of polypropylene applications, provided the resin is well adapted. A number of problems remain still unsolved, but joint effort of resin producers and machine manufacturers will certainly generate improvements and new solutions.

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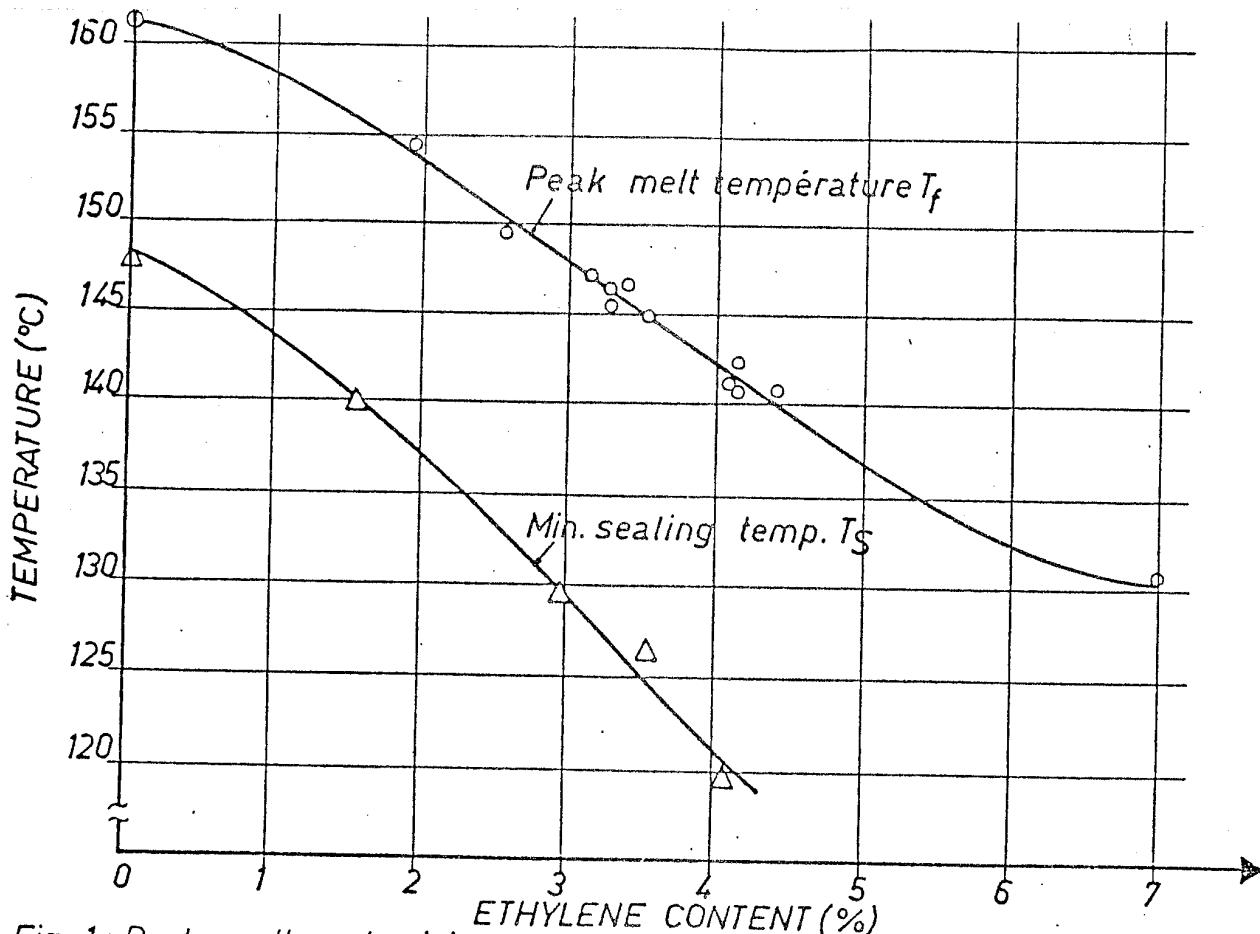


Fig 1: Peak melt and minimum sealing temperature as a function of ethylene content in E/P random copolymers.

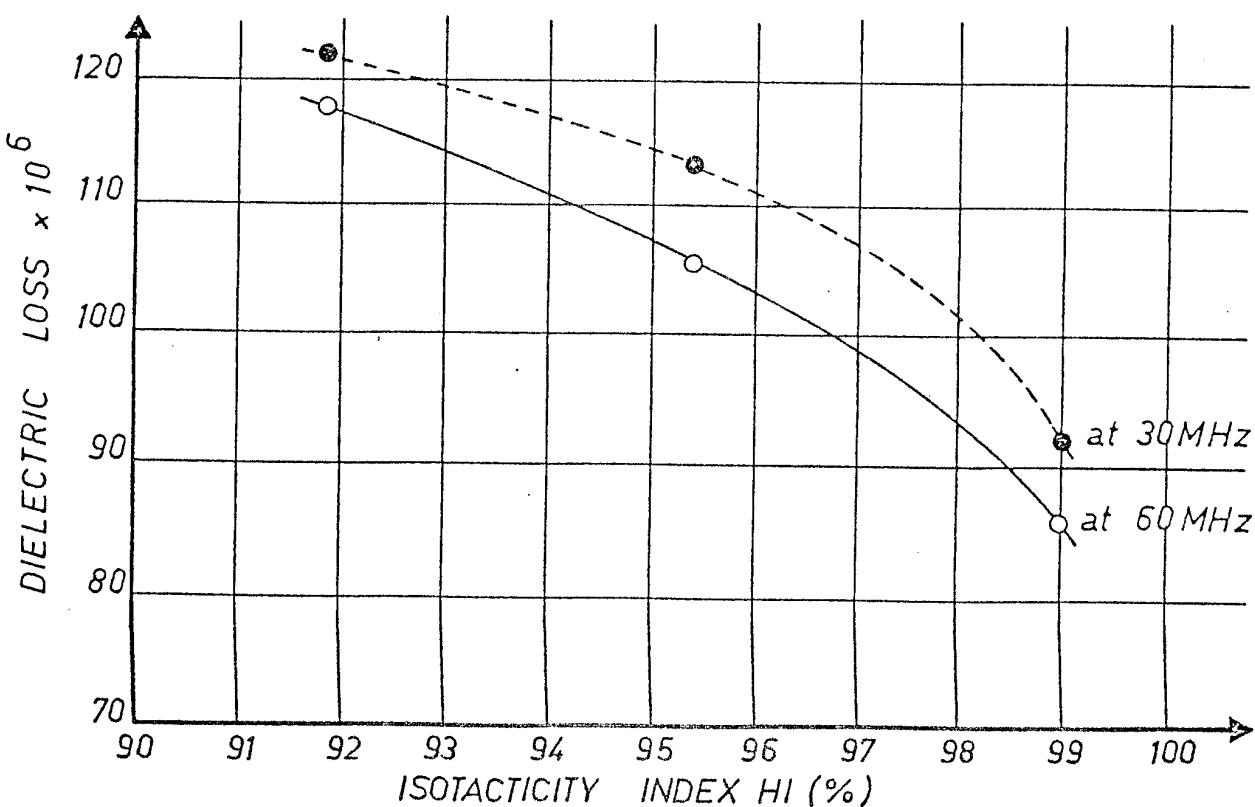


Fig 2 : Influence of isotacticity index (heptane insolubles) on dielectric loss for PP.

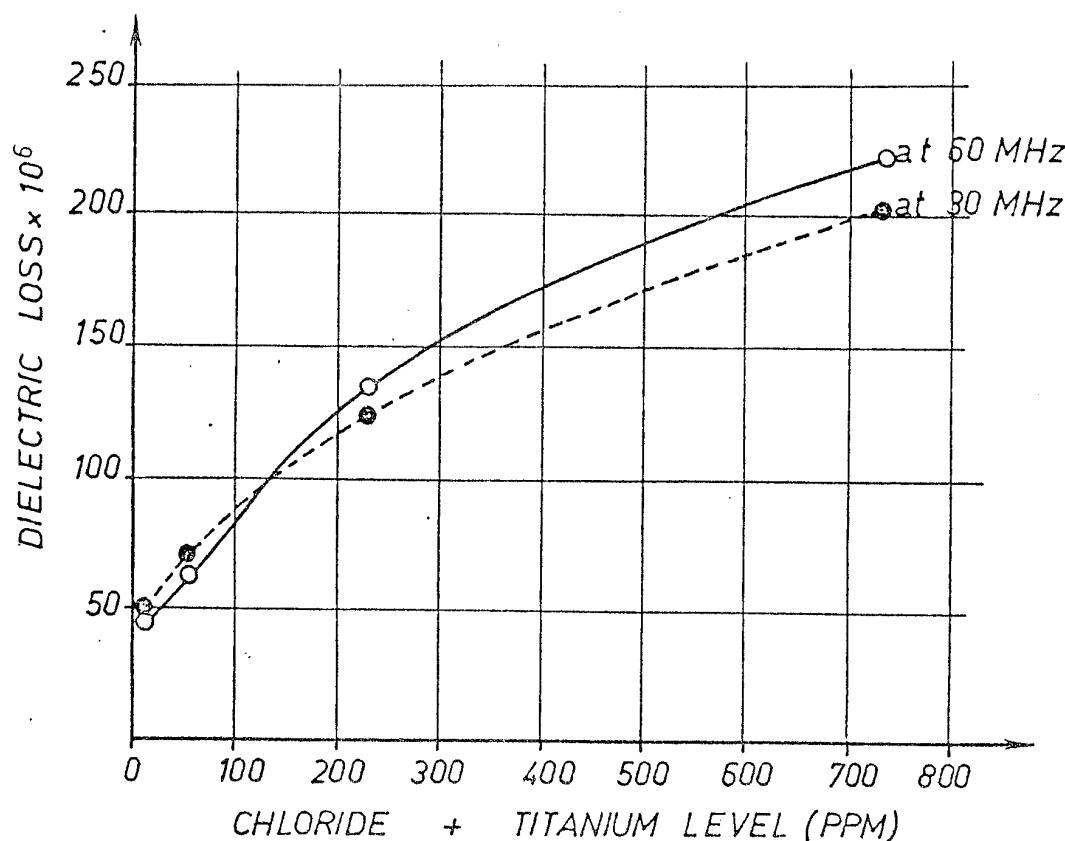
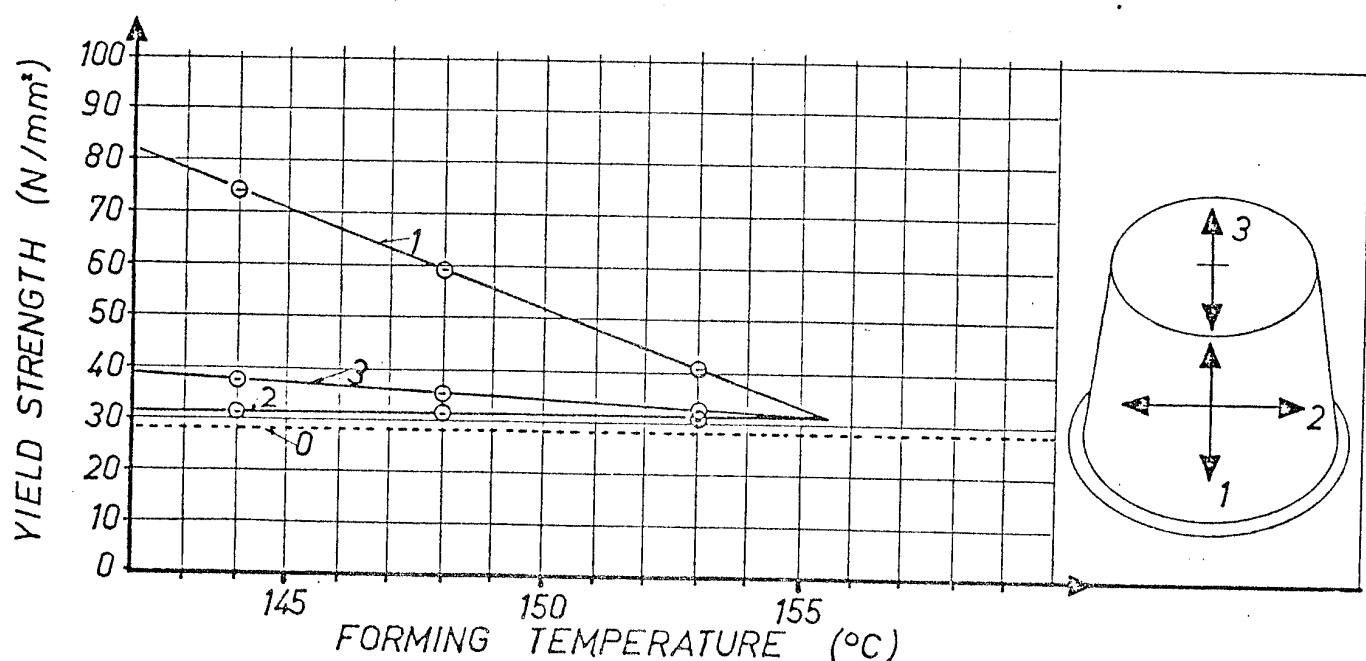
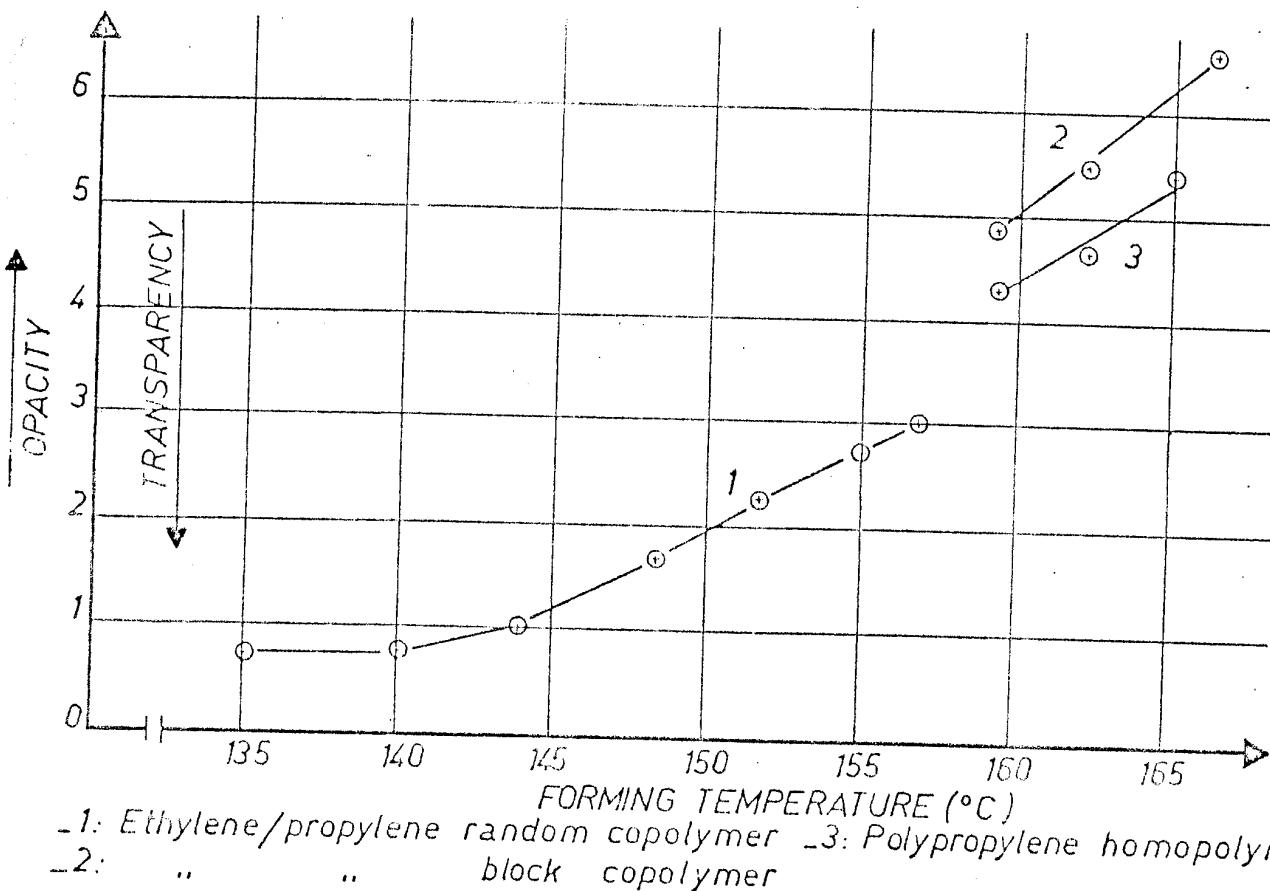


Fig 3 : Dielectric loss as a function of residual chloride and titanium level in PP



- 0: Extruded unformed sheet (1mm thick)
- 1: In lengthwise direction in the middle of the mono-axially orientated side wall
- 2: In transverse direction in the middle of the side wall
- 3: In the center of the (slightly biaxially orientated) bottom.

Fig 4 : Yield strength as a function of sheet forming temperature.



-1: Ethylene/propylene random copolymer -3: Polypropylene homopolymer
 -2: " " block copolymer

Fig 5 : Transparency as a function of sheet forming temperature.

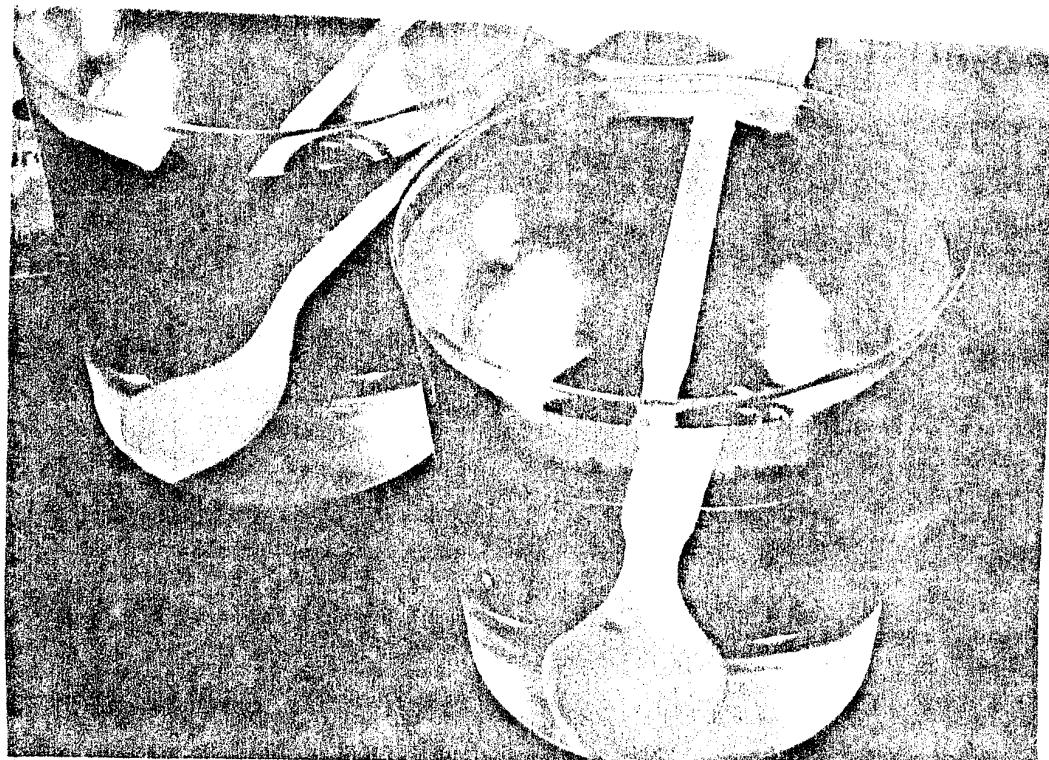


Fig 6 : Containers thermoformed from a 1mm thick ethylene/propylene random copolymer sheet.

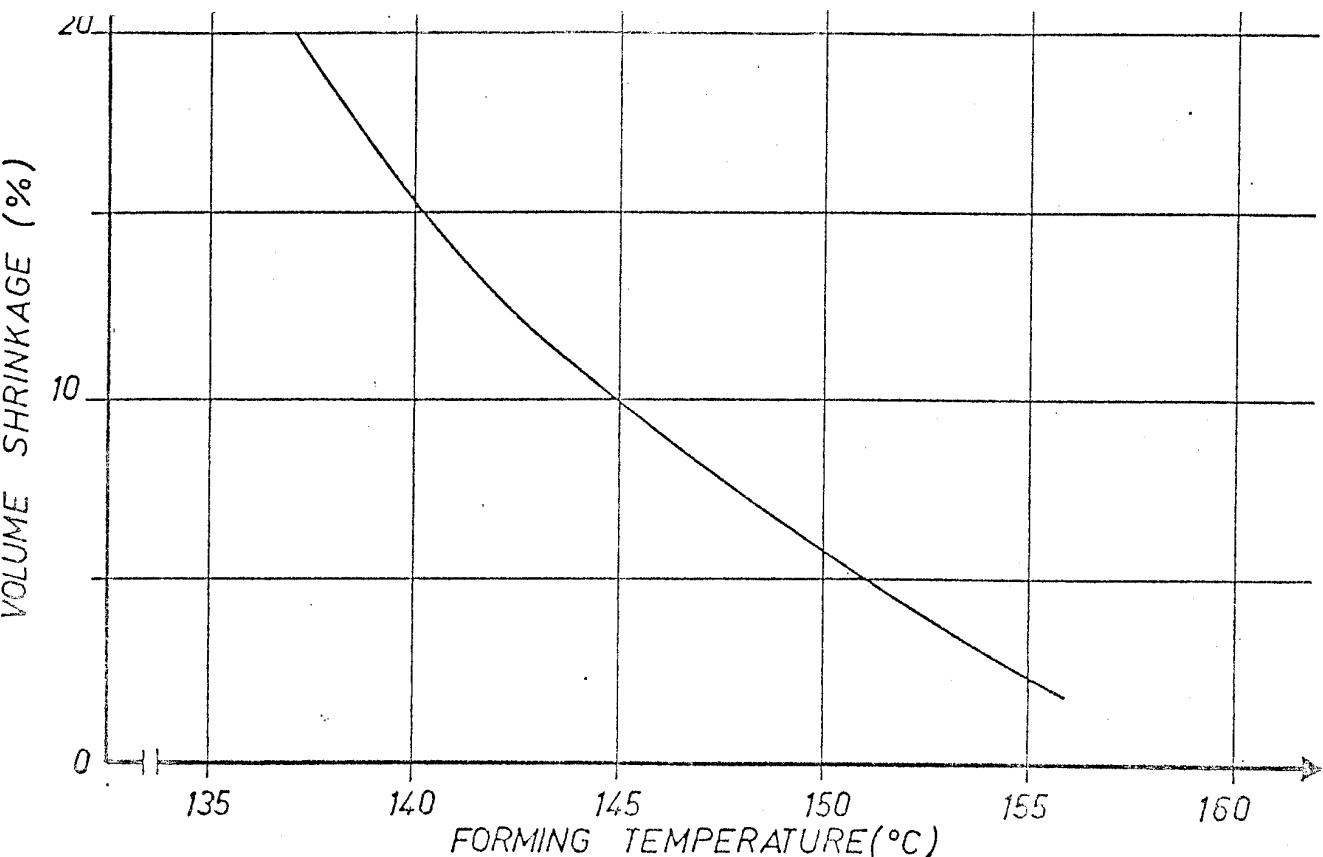


Fig 7 : Volume shrinkage as a fonction of forming temperature for a random copolymer after one hour at 130° C.

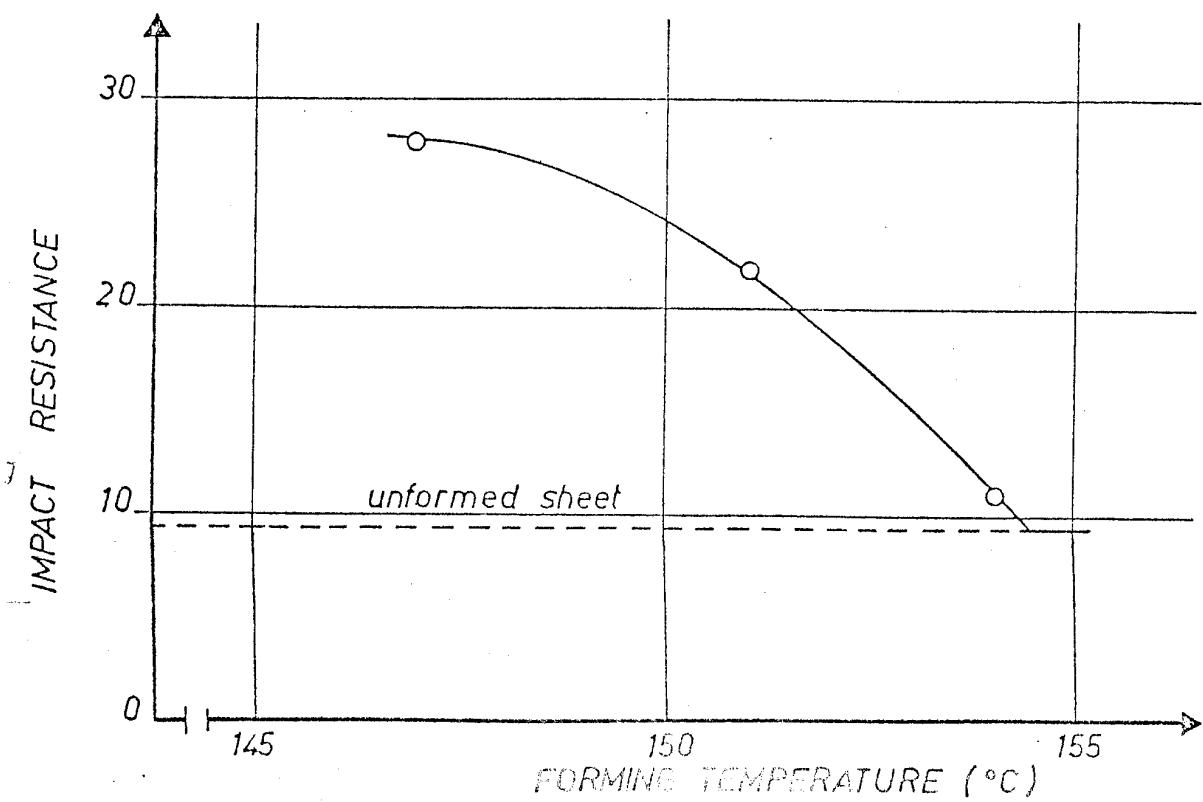


Fig 8 : Impact resistance of the bottom of containers formed from E/P random copolymer sheet as a function of forming temperature.

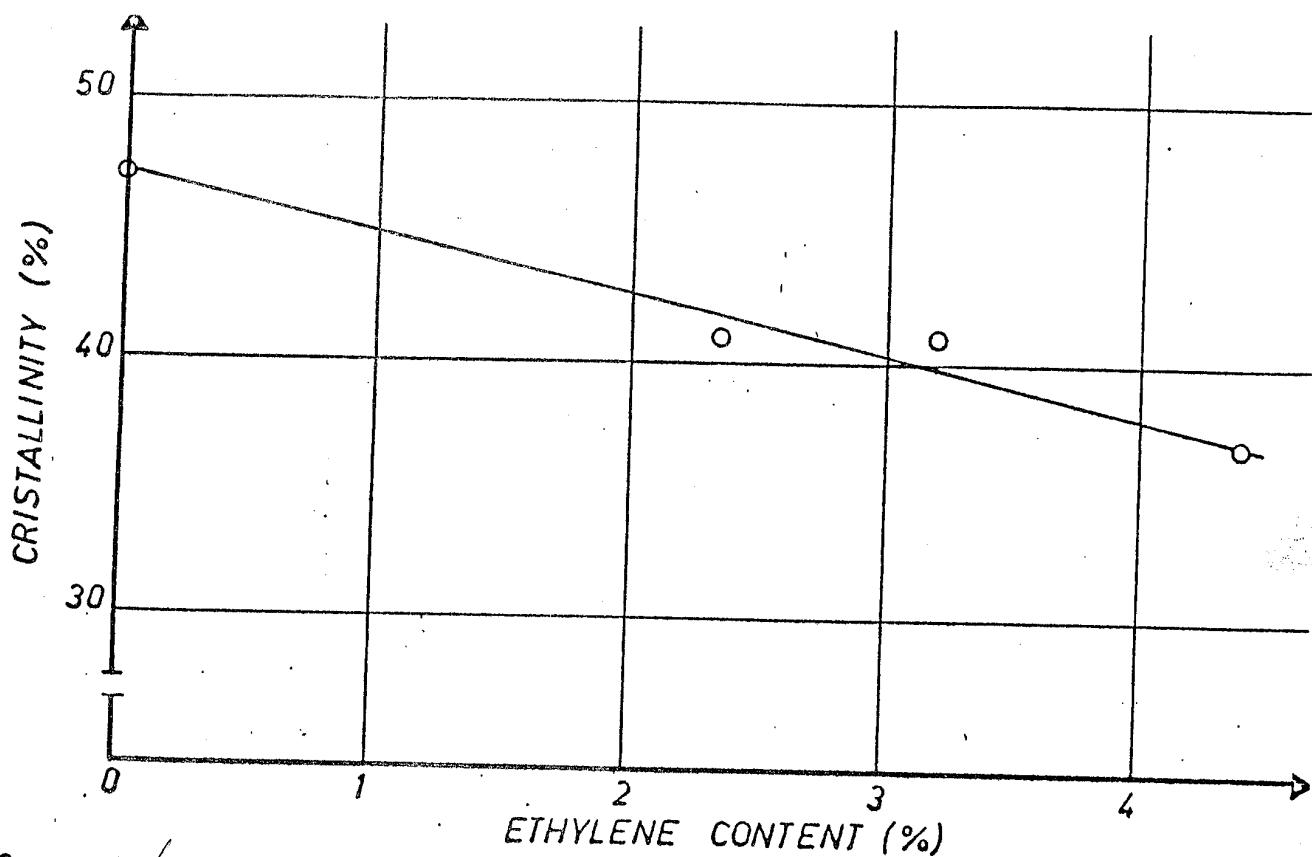


Fig 9 : Crystallinity of E/P random copolymers as a function of ethylene content.

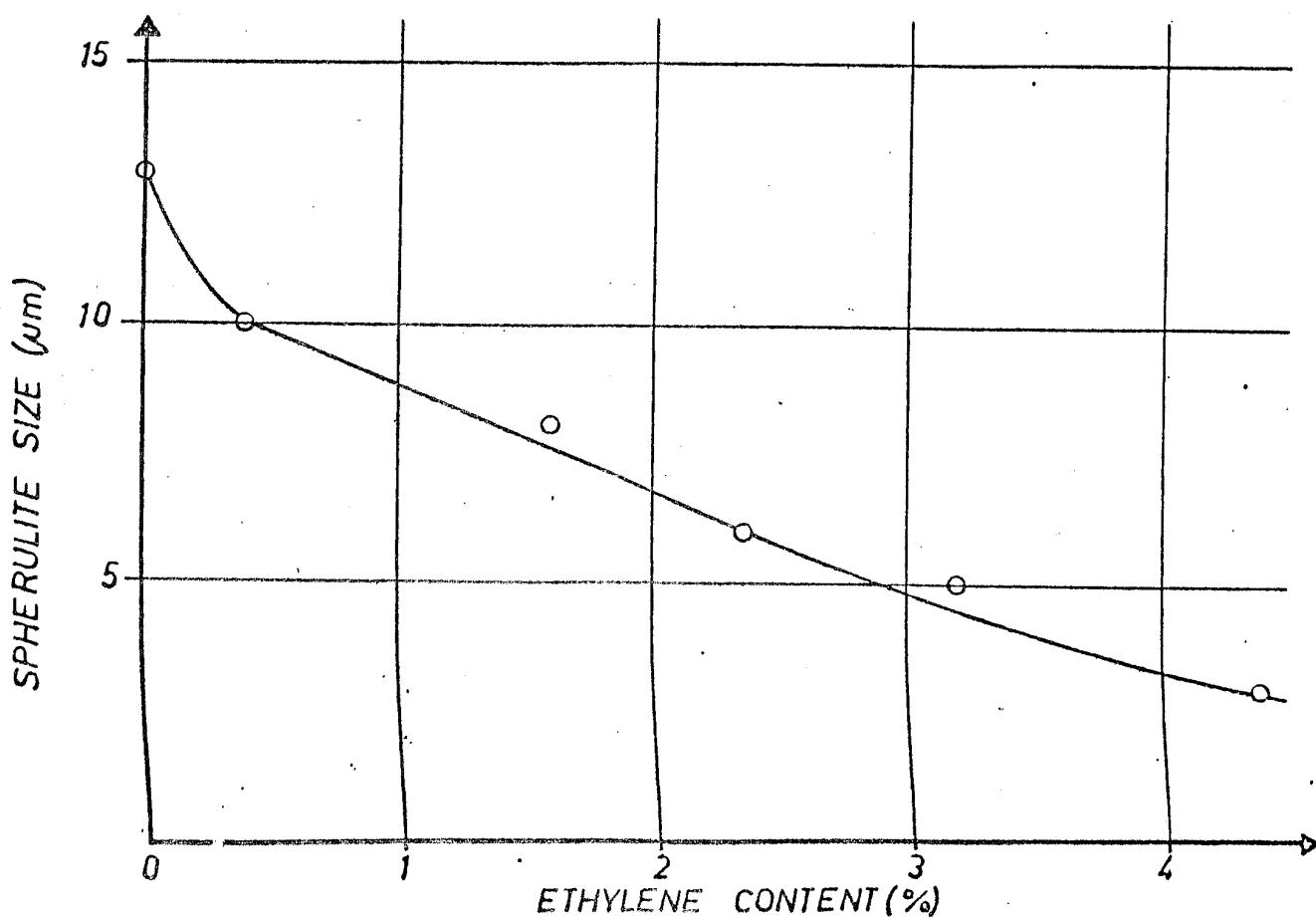


Fig 10 : Average spherulite size of E/P random copolymers as a function of ethylene content.



Fig 11: Peanut oil bottle blown from E/P random copolymer on conventional HDPE equipment.



Fig 12: Ethylene/propylene random copolymer bottles.
Right: Stretch blown from an injection moulded preform
Stretch ratios lengthwise 1.85: 1, radial 3.1:1
Left : Blown on conventional HDPE equipment.

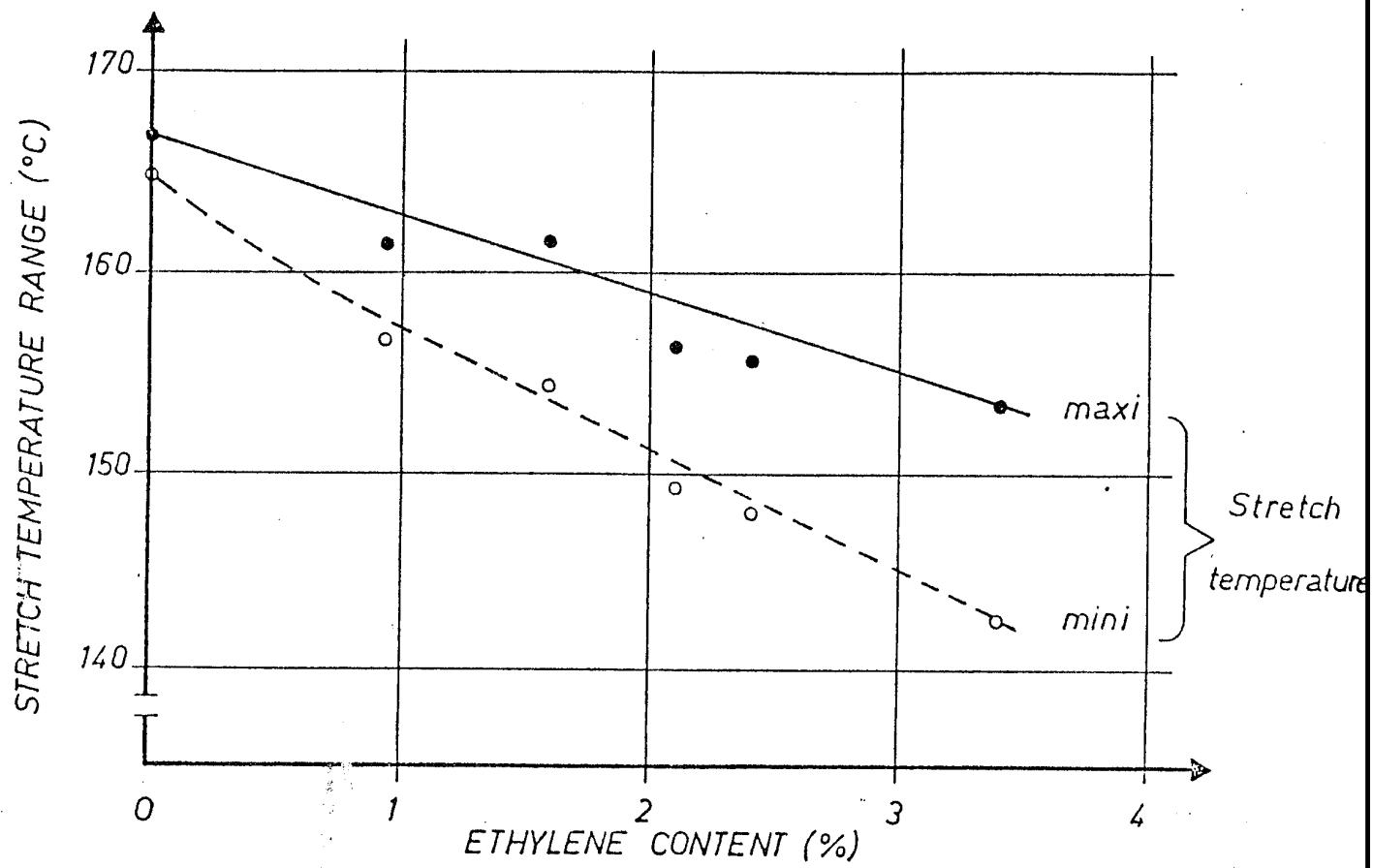


Fig 13 : Stretch temperature range for stretch blown E/P random copolymer bottles as a function of ethylene content.

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POLYOLEFINS SHARE IN PACKAGING AREA

Dr Michel CHRISTEN

Packaging Consultant

57, ruedu Général de Gaulle
F 91240 Saint Michel sur Orge

POLYOLEFINS SHARE IN PACKAGING AREA

Briefly summarized, the overwhelming success of plastics in packaging is due to three main reasons:

- First of all, they succeeded in reconciling antagonist properties, or rather reputed to be so, such as: Impermeability, transparency, flexibility, stiffness and lightness.
- Secondly they have made possible both see-through and one-way packages favoring developments of mass production, mass distribution and mass consumption; by the same token, they originated new handling and grouping techniques.
- Last, but not least, they lend themselves to partly or fully integrated production of containers.

Being unable to give an exhaustive outline of the whole properties of plastics in a short survey, we have selected some that are thought to be the more significant as use properties in packaging:

- Creep under load (stacking behaviour)
- Impact strength (drop and shock resistance)
- Optical clarity (product visibility)
- Transmission of gases and vapours (protection against oxydation and humidity)

These bulk properties depend, in fact, on what is happening at the microscopic level. Considering the classic maxim "a chain is no stronger than its weakest link", all the molecular chain within covalent bonds are operative should display the same mechanical strength approximately twenty times higher as they do. That gap evidences properties are mainly governed by intermolecular structure, that is to say, by magnitude and distribution of attractive forces between molecules.

Intramolecular structure and intermolecular structure are essentially determined by underlying physico-chemical properties and accordingly involve both energetical and geometrical aspects. As we know, systems containing one or several entities tend to arrange themselves so that their energy content is minimum.

For metals, the three-dimensions arrangement of atoms (i.e. the crystal) results from simple packing of spherical units with spherically distributed bonds; the resulting three basic structures (cubic close-packed, cubic body centred and hexagonal-close packed) account for the high densities of metals and their remarkable mechanical behaviour (notably their ductility).

When long molecules with irregular and complex configuration are concerned, they try to link one to another by a maximum of reversible bonds (Van der Waals bonds); these interaction forces between macromolecules, or between segments of the same molecule arise only if interacting sites are accessible, and then the forces become stronger up to a maximum corresponding to the ideal closest approach of the interacting sites.

Obviously, it becomes more and more difficult to arrange macromolecules in a regular way as their inherent "tortuosity degree" increases, and the result is that ordered regions (crystalline) and disordered regions (amorphous) co-exist in the polymer matrix.

For instance, in "pure" polyolefins, namely linear polyethylene, chains are held together only by weak forces (London forces), but the weakness of forces (0.5 - 1.0 K.cal/g.mol.) is somewhat counterbalanced by a great number of effective active centers. That gives to high molecular weight polyethylene a relatively high melting point ($\theta_m \approx 140^\circ\text{C}$), far below that of polytetrafluoroethylene ($\theta_m \approx 327^\circ\text{C}$) although they show a similar cohesive energy! In fact, the difference in thermal behaviours comes from difference between chain flexibilities.

Besides, a low interaction energy and a high symmetry level of the straightened macromolecule lower the potential energy barrier allowing one chain to glide by another, or allowing the relative shifting of complete layers of molecules along a "slip-plane".

This situation ,with a least symmetry degree is quite similar to that occurring in metals and seems to give a fairly good explanation of creep properties exhibited by the two unique highly symmetrical polymers: Polyethylene and Poly-tetrafluoroethylene.

Going on further, as a crystalline material undergoes a percussional stress(i.e. a stress localized in space and in time) its macromolecular constituents respond in a cooperative way either by reversible deformation(energy dissipation through vibration modes), either by irreversible deformation(creep or rupture); here we think that creep mechanism are likely responsible of good impact behaviour of Polyethylene and Polytetrafluoroethylene.

A less symmetry degree leads to a more disordered state (glassy state), but this state may be obtained from molten materials by quenching. As we know, for the same polymer, specific volume and enthalpy of amorphous phase are larger than those of crystalline phase which is postulated as the more stable. In other words, glassy state differs from crystalline state by a larger so-called "free volume" and many more "pre-stressed bonds". Therefore, amorphous plastics contain sub-microscopic germs of cracks and their chains respond to sudden stress in a non-cooperative way and, as a result, they are shown to be more impact sensitive than crystalline one .

Such is, shortly and schematically, how can be depicted crystalline and amorphous polymers, and precisely here lies the "cleavage" between polyolefins and other polymers.

As shown in the table, hereafter, crystalline polymers undergo a more dramatic change of their properties near the transition temperature.

	CRYSTALLINE POLYMERS	AMORPHOUS POLYMERS
Transition temperature	θ_m	θ_g
Order level change	High	Low
Viscosity change	High	Low
Specific gravity change	High	Low
Optical clarity change	High	Low

On a practical view point, a low viscosity change, for instance makes easier thermoforming of plastic sheets and consequently up to 95% of "thermoformed items" market is held by amorphous polymers.

In the same way, they are also the "workhorses" for thick-walled transparent containers because no clarity change occurs on slow cooling.

As expected, both families have tried to get competitor's characteristics, and the resulting plastics are something like hybrids with a "microcrystalline structure embedded in an amorphous matrix".

First of all, Polyolefins are now transparent through control of crystallites growth either by shortening of linear sequences (Copolymerisation, branching, cross-linking), either by shock cooling (Chill-roll, cold blowing, water bath) or by both. As we know, crystallites are responsible for light scattering, but fortunately their action vanishes as their dimensions are kept slightly below that of incident light wavelength.

On other hand, by controlling crystallinity we restrain the spread of a spherulitic superstructure leading to a grain structure, as for metals. Thus spherulites growth rejects and concentrates defects (impurities, ties, entanglements, branching) at grain boundaries, creating voids of least strength and therefore increasing brittleness of materials.

In low density polyethylene, copolymerisation, with polar monomer (i.e. acrylic acid, vinyl acetate) also improves cold-flowing resistance and stickiness. Likewise in high density polyethylene copolymerisation with butene-1 (2-5%) give better creep and stress-cracking resistances.

Polypropylene exemplifies clearly how intramolecular order (orientation of side groups) affects intermolecular forces. Atactic form is a rubber-like material while isotactic form is semi-crystalline (60% crystallinity); a more rigid back-bone originating in a less randomness degree (configurational energy) raises the melting point up to 170°C, value quite satisfactory for hot-filling and sterilization.

The effect of side branches seems to reach its maximum with polybutene-1 obtained in its highest crystalline form (75-80%). Polybutene is a strong, rigid -but flexible- material with excellent resistance to hot-creep and stress-cracking.

An other way of improving hot-creep in molten state and related properties as tear strength lies in erecting a tri-dimensionnal network leading to:

- Irreversible structure by irradiation or chemical cross-linking (Cross-linked PE films).
- Reversible structure by thermolabile ionic bonding as in Ionomeric materials which duplicate silica glasses structure.

Conversely, polymers with an atactic structure or with a long repeating "monomer unit" are generally found in a "naturally" occurring glassy state; nevertheless under external action as blowing, stretching in melt or by cold drawing, chains become aligned and their slip one by another favours settlement of a more stable extra-molecular order.

Mono-orientation (fibers) and bi-orientation (films and containers) are means that induce a more "sympathetic" and collective behaviour of macromolecules and therefore improve mechanical and transmission properties.

The orientation efficiency depends on macromolecules symmetry and on their interaction level; for instance, bi-orientation imparts better properties to polyethylene-terephthalate and polyacrylonitrile (gain up to 15%), but properties of polyvinylchloride are not appreciably changed by the same treatment. Polyamides, which are amorphous or randomly polycrystalline, become more crystalline on stretching and remain so, their chains being held parallel by a strong H-bonding.

In barrier properties area complexity arise not only from structure but also from nature of diffusing species which interact more or less with macromolecules. The general principle "like dissolves like" applies to transmission properties in the form "like permeates like".

For low interacting species, structure compactness is the prominent parameter; the higher is the density, the lower is the permeability. Having, by essence, low densities polyolefins are poor barrier materials comparing to others.

Crystallinity seems to have an influence only as providing a density increase. As diffusion takes place preferentially through amorphous regions, all means favouring interactions between chains, like cross-linking, biorientation, ... improve tightness.

When the permeant has a permanent dipole moment, and more over, when it is able to develop strong H-bonding, as water does, a subsequent cohesion loss and a swelling occur that enhances the diffusion of permeant. Then, polyolefins join other common materials and even take advantage on those that undergo a water plasticization, like polyamids, cellulose and derivatives, polyvinyl alcohol, despite they exhibit excellent barrier properties to dry gases, pertaining to their densities.

Permeation rates of organic vapours are governed by the "similarity principle", for instance in polyolefins, permeabilities of organic vapours are lowest with strongly polar materials and rise from alcohol to hydrocarbons.

Fair barrier properties connected with excellent inertness and very low solubility offer to polyolefins many possibilities in industrial and foods contact applications.

As shown in next table, the competition field is n't restricted to a plastic/plastic substitution, and among the numerous successes of polyolefins, the most outstanding one is, may be, their past breakthrough in handling crates and boxes where they progressively led to wood "eradication". The main reasons of such success are summarized hereafter.

TWELVE BOTTLES (1.00-1.25 l.) CRATE

MATERIAL	WOOD	PE H.D.
STRUCTURE TYPE	MULTICOMPONENT	MONOLITHIC
JOINING ELEMENTS	NAILS/STAPPLES	-
TARE	Changing on hum.	Constant
TOLERANCES	Broad	Narrow
STACKABILITY	Poor	Excellent
WEATHERING	Swelling & Corr.	Good
AGING	Splitting	Excellent
CLEANING	Difficult (mould/r.)	Satisfactory
MAINTENANCE	Necessary	No
ASPECT	Poor	Good
RECYCLING	Difficult	Possible
LIFE-SERVICE	4-6 Years	> 16 Years

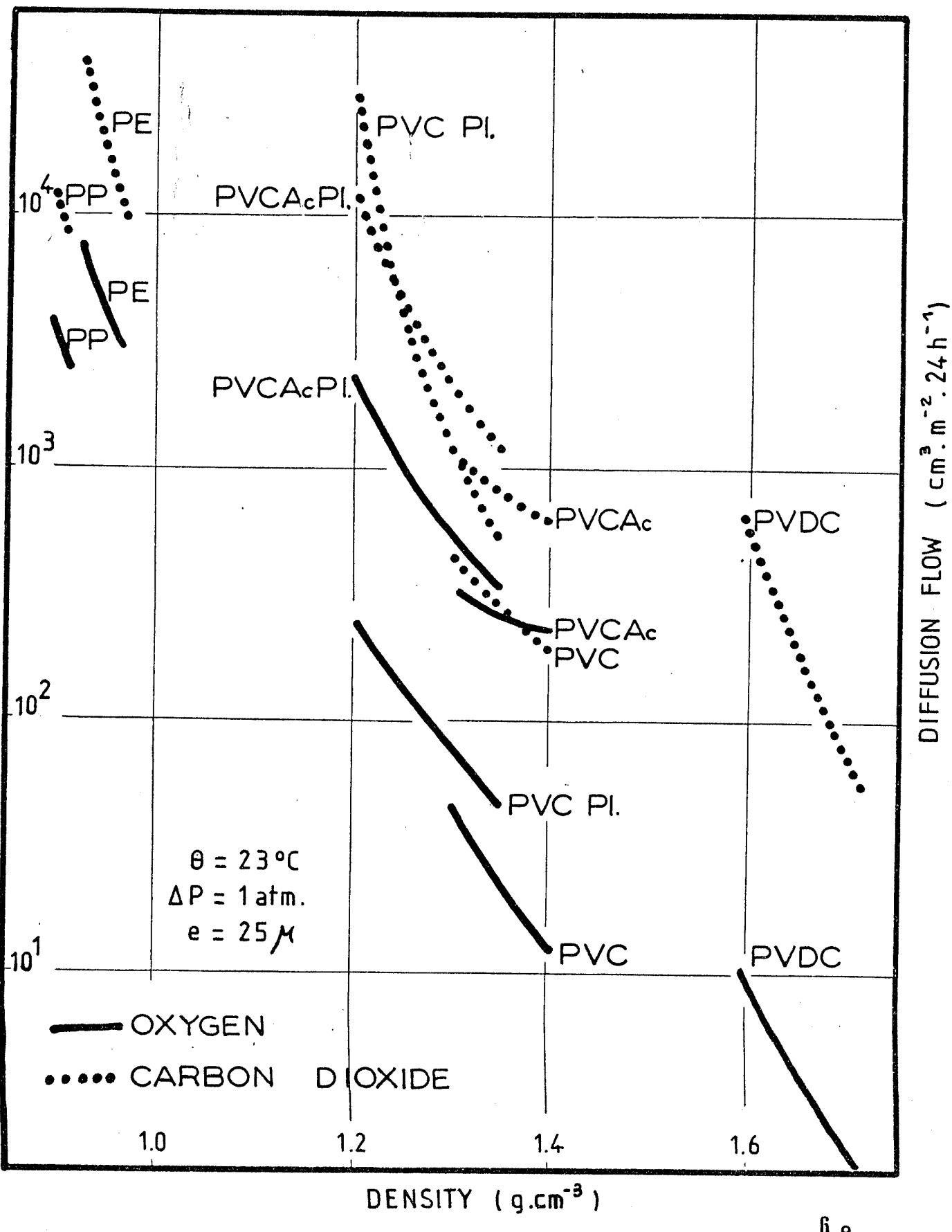
In a different field, that of "Changing geometry films" covering both "memory films" -or shrink films- and "elastic films" -or stretch films-, polyolefins have revolutionized wrapping and packaging practices.

Previously, protection of goods was carried out, only, through a "blind" and sometimes redundant method : a shipping container with adequate cushioning. The see-through clear films of polyolefins have made possible development of a "psychological" method : becoming aware of product fragility

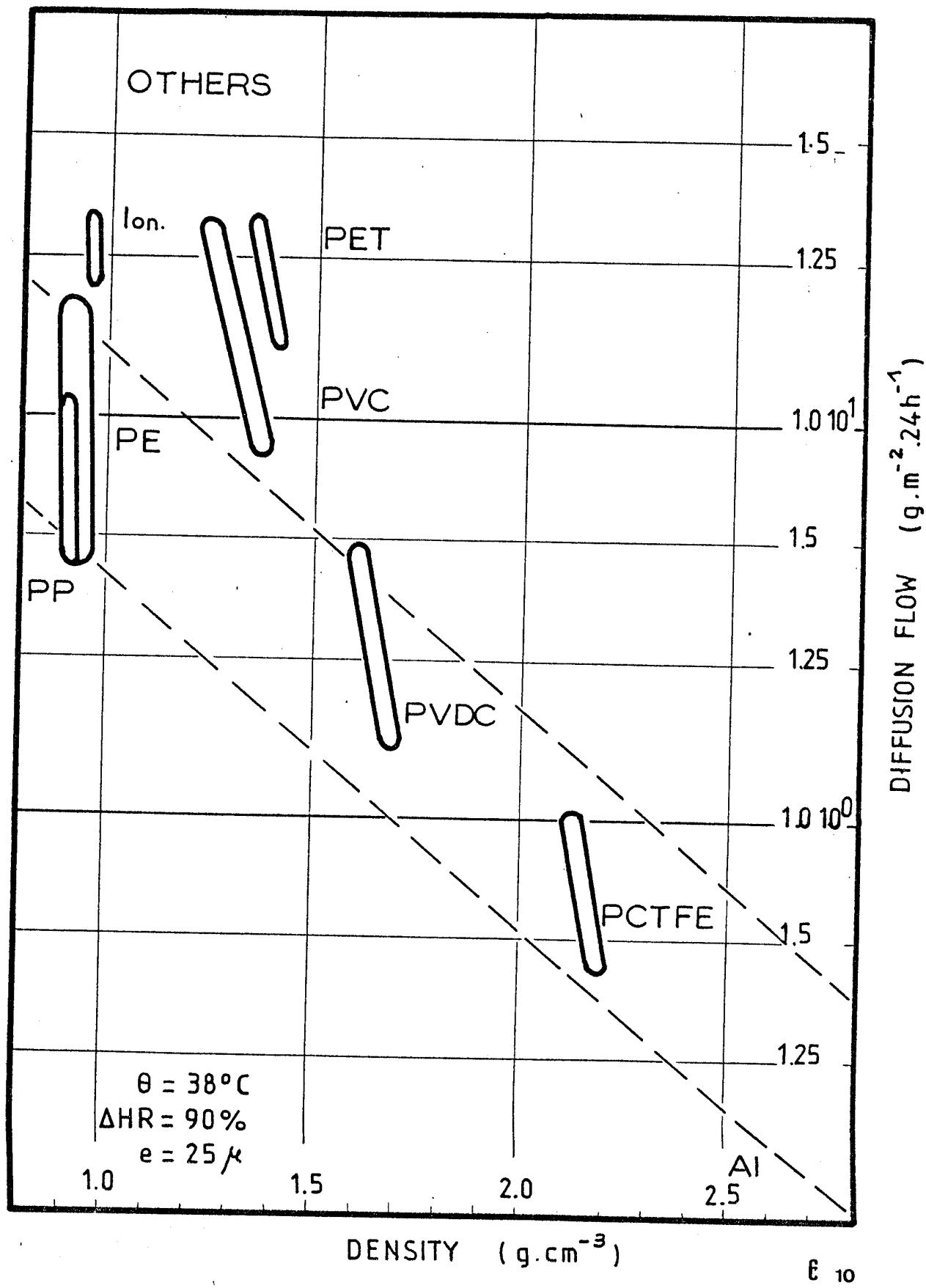
handling and transport operators treat it with the care it warrants.

In the course of our lecture, we have intentionally dismissed the underlying economical aspects despite they are present in life-time service, maintenance and damage prevention considerations. Obviously, although they become more and more sophisticated, polyolefins, draw advantage, and will keep it, from their low prices due to direct synthesis from key chemicals; but their successes mainly lie on a combination and a balance between various properties fitting well with needs.

DIFFUSION FLOW OF GASES



DIFFUSION FLOW OF WATER VAPOUR



SUBSTITUTION CHRONOLOGY

NEARLY ACHIEVED SUBSTITUTIONS

CHALLENGING MATERIAL	REGRESSING MATERIAL	APPLICATION
POLYSTYRENE	GLASS	Yoghourt
POLYVINYL CHLORIDE	GLASS	Minerals, oil & vinegar
POLYETHYLENE H.D.	WOOD	cosmetics,...
POLYETHYLENE H.D.	GLASS	Bottle crates
PE L.D. coated	GLASS	Milk, liquid soaps,
PAPER BOARD		cosmetics
		Milk

RUNNING SUBSTITUTIONS

CHALLENGING MATERIAL	REGRESSING MATERIAL	APPLICATION
PVC & PET	GLASS	Carbonated water
POLYPROPYLENE	NATURAL FIBERS	Heavy duty bag
PP & PET	METAL	Strapping

STARTING SUBSTITUTIONS

CHALLENGING MATERIAL	REGRESSING MATERIAL	APPLICATION
POLYPROPYLENE	CELLULOSIC FILM	See-through packages
POLYETHYLENE H.D.	METAL	Pails & high cap. drums
POLYETHYLENE H.D.	WOOD	Fruits & veget. crates
POLYETHYLENE H.D.	PAPER	Meat, fishes, backeries,

FUTURE SUBSTITUTIONS (?)

CHALLENGING MATERIAL	REGRESSING MATERIAL	APPLICATION
PET & PVC	GLASS	Beer, soft drinks
POLYPROPYLENE	POLYSTYRENE	Fresh dairy products
POLYETHYLENE H.D.	WOOD	Pallets
PE L.D. Coated	POLYETHYLENE H.D.	Milk
PAPER BOARD	CORRUGATED BOARD	Boxing
POLYSTYRENE/KRAFT	KRAFT	Heavy duty bag
POLYBUTENE		

U.S. TECHNICAL TRENDS IN THE AREA OF POLYOLEFINS

Invest

Q107

R. G. HAYTER

SHELL DEVELOPMENT COMPANY
WESTHOLLOW RESEARCH CENTER
HOUSTON, TEXAS

SOCIETY OF PLASTICS ENGINEERS

First EURETEC

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U.S. Technical Trends in the Area of Polyolefins

In recent years, the growth in consumption of polyolefins in the U.S. has exceeded that of the overall economy by a wide and consistent margin (1st slide). For example, low density polyethylene enjoyed an annual average growth rate of 14% from 1975 through 1978, high density polyethylene 21% and polypropylene 17% in the same period.) By contrast the consumption of all plastics grew about 16% and the GNP by 4.2%. These relative growth rates and other more detailed assessments show that polyolefins along with other plastics are making rapid penetration into the materials economy of the U.S. by replacement of traditional materials of construction such as wood, glass, paper and metal.

Most forecasts project a continuation of the penetration by polyolefins, although at somewhat lower growth rates than the historical rates. LDPE has a projected growth of 6% AAI which appears to be significantly affected by anticipated tightness in supply to the market place for the next several years, as several producers re-evaluate construction projects in the light of the current economic picture and Union Carbide's announcement of plans to build one billion pounds of linear low density polyethylene. More on this process later. HDPE, on the other hand, is freely available with current operating rates representing about 76% of nameplate capacity (5.4 billion pounds) and growth is projected in the region of 8-9%. Polypropylene is enjoying the benefits of a number of newly installed, excellent quality manufacturing facilities and growth rate projections as high as 13% are being made, although 8-10% appears more likely.

In addition to the commodity polyolefins, lower volume materials such as poly(butene-1) and ultrahigh molecular weight polyethylene show high growth rates and increasing acceptance in specific applications.

The factors affecting these growth trends are many and various and too numerous to discuss in detail in this presentation. However, it is appropriate to refer to factors other than the technical ones which are the main purpose of this presentation (2nd slide). The U.S. trend towards the cracking of heavy liquids (naphtha and gas oil) as the process of choice for ethylene manufacture is expected to result in increased availability of (and potentially lower cost) by-product propylene and butylenes including butene-1. In addition, the increasing cost of energy and the enhanced value of aromatics in non-leaded gasoline appear generally to favor the cost structure of polyolefins versus other major plastics such as the styrenics and polyvinylchloride. Environmental factors have also shown less adverse effect on polyolefins than some other materials; longer term it may also be of significance that polyolefins can be burnt for potential energy recovery more economically than other materials of more complex constitution.

Of more direct interest today are the current technical aspects of polyolefins and I would like to discuss recent trends in manufacturing technology, particularly the simpler processes available from advances in catalyst and process technology. Prominent among these are the new fluidized bed processes for linear low density polyethylenes and the non-deashing, non-extracting processes available through the highly active Ziegler-Natta type catalysts for manufacture of other polyolefins.

New products are now becoming available from these new processes and linear low density polyethylenes are seeking application in wire and cable and injection molding. Also prominent are new high flow grades of polypropylene and HDPE for thin wall injection molding. New and improved polybutylenes are also increasing the penetration of this new material into increasingly demanding segments of the piping market and expanding its use relative to the polyethylenes as a film resin. New products are also being developed to increase the adaptability of polyolefins to processes formerly used for other materials. Current examples include polyolefins for stamping in machinery formerly used for manufacture of metal parts for the automotive industry and thermoforming which has formerly been more widely applied to the non-crystalline thermoplastics. Solid phase forming technology is now recently commercial in the U.S. and products are emerging for this new process.

Manufacturing Technology

Linear Low-Density Polyethylene

During the last 1-2 years much interest has been generated by the new or modified existing processes for producing linear low density polyethylenes. Since Union Carbide's announcement in late 1977 of a new low pressure gas phase process for LDPE,²⁾ other producers have indicated their ability or intention to manufacture similar or related products in existing or modified high density plants using a solution or slurry process. The particular interest in the Union Carbide process is the suggestion that such a process is close to the "ultimate" process for a major thermoplastic. This process is compared with a conventional high pressure process (3rd slide). Many of the advantages of the process derive from its inherent simplicity in both reactor conditions and recovery systems resulting in significant expected reductions in capital costs for a new facility of up to 50%. The formation of polyethylene in the reactor as a granular solid avoids the need for stripping and pelletizing, both energy intensive operations. This new granular form is suggested to have advantages in ease of handling such as in dry blending. In some applications, however, this product form could cause problems in reduced homogeneity and dispersion of additives compared to that characteristic of conventional mixing and pelletizing.

Another major difference is that the product composition and structure is inherently different from that of conventional low density polyethylene. Low density (and lower crystallinity) is achieved by copolymerization (with propylene or butene-1) in the presence of a supported transition metal catalyst rather than by long chain branching typical of the free radical mechanism of the conventional process. The increased linearity with uniform, short branches and narrower molecular weight distribution apparently gives rise to significant performance differences (Slide 4). The improvements in stiffness, toughness and stress crack resistance offer advantages over conventional resins in particular applications, especially wire and cable and injection molding which together make up about 18% of the LDPE market. To date, however, the processing limitation³⁾ and poor optical properties associated with this type of product (Slide 5) have inhibited penetration of the large film and sheet market. Whether the new processes can be adapted to produce products with rheology more closely matching LDPE remains to be seen.

Polypropylene

Current trends and discoveries in polypropylene manufacturing technology suggest that the ultimate process for polypropylene may also be close to reality. However, the recent surge in new capacity additions in the U.S. were mostly based on conventional process technology. The increasing use of highly active catalysts in currently existing plants and the first U.S. plant based on gas-phase technology developed in Europe by BASF are indications that a race is on to identify the ultimate process. I wish today to focus on trends in catalyst technology since this, just as in polyethylene, is potentially the key to the next generation of simplified low cost processes which would eliminate the use of such process steps as catalyst removal, atactic washing and pelletization. Slide 7 shows the dramatic advances which have been made in Ziegler-Natta type catalysts based on titanium trichloride - aluminum alkyl chemistry⁴⁾ since the early discovery of isotactic polymerization in the mid-1950's.⁴⁾ Since the first discovery, the industry catalyst workhorse has been the α/γ -modification of $TiCl_3$, prepared by reduction of $TiCl_4$ with aluminum metal, organoaluminum compounds or hydrogen in the region of 3000 lb. polymer per lb. Ti per hour appear to be the limit for this type of catalyst. Processes based on these catalysts therefore incorporated aqueous or organic catalyst removal steps which also removed the undesirable soluble amorphous polymer so that the final product was able to meet the product quality required by such applications as tape, fiber, and electrical film. Process improvements in the sixties mainly focused on improvements in catalyst selectivity by the use of additives to control the wasteful production of unwanted atactic polymer.

In the seventies major improvements in catalyst activity and selectivity have been made. As illustrated by the catalyst described in Solvay patents, this appears to be achieved by treatment of a conventional type catalyst with an ether (dissolving co-crystallized aluminum trichloride), followed by treatment with $TiCl_4$ below $100^\circ C$. This yields a $\alpha/\gamma TiCl_3$ type catalyst with higher surface area and porosity and aluminum free. A 3-4 times enhancement in activity, is gained with retention of good selectivity. The granular form of the catalyst is retained in the final replicated polypropylene particle and products based on this technology are now commercially available in the U.S. from a process which is described as "non-deashing".

More recently, Mitsui Petrochemical amongst others have patented a different type of catalyst in which a titanium chloride is incorporated into a magnesium chloride crystal structure. When polymerizations are conducted with suitably high amounts of organoaluminum cocatalysts (200-400 Al/Ti), rather than the lower ratios (2-5 Al/Ti) of the conventional catalysts, remarkably high titanium based activities (up to 150,000 lb. PP/lb Ti/hr) are obtained. Although these catalysts are designed to make extremely efficient use of titanium, the total inorganic ash remaining in the polymer is still higher than can be tolerated for the more stringent product applications. Catalysts based on this technology are now under active development in the U.S. Specific comparison of the comparative performance of these catalyst types are given in Slide 8.

The original Ziegler-Natta catalysts consisted of bulk crystalline $TiCl_3 \cdot 1/3 AlCl_3$ of low surface area and low porosity containing a limited number of potentially active titanium catalyst sites with suitable vacancies. Treatment with ethers followed by $TiCl_4$ is thought to open up additional catalyst sites and to give a more porous structure, essentially aluminum free. The $MgCl_2$ -containing catalysts are thought to contain titanium chloride supported on the surface of a $MgCl_2$ lattice containing double or two adjacent single vacancy sites. Maximum use can thus be made of catalytically active titanium sites. In each case, the role of the organoaluminum cocatalyst is critical (and controversial) but is clearly an important factor in control of titanium activity and selectivity.

It is clear from the above discussion that significant current developments are aimed at further simplification of polyolefin processes through catalysts advances. By taking advantage of product properties and physical form available from such improved processes, products are being developed for new and existing applications.

Products and Applications

In the introduction, the high growth rates of polyolefins were attributed in part to the displacement of traditional materials. New developments continue to assist these trends in a number of industry segments. Some examples will be reviewed from the packaging industry (replacement of metals, glass, paper, cellophane), automotive (metal replacement) and construction (replacement of steel and copper).

High Flow Polyolefins

One of the more exciting new material developments in the U.S. has been the rapid emergence of a large number of new high flow injection molding polyolefins from virtually every major producer.⁵⁾ Polypropylenes of 12-35 melt flow and new HDPE resins of 20-80 melt index have been developed for high speed injection molding applications in thin-walled parts. The higher flow characteristics offer a variety of processing benefits (Slide 9) such as lower processing temperatures, faster cooling times and overall cycle time reduction. These benefits translate to improved productivity of the injection molding process and increased flexibility of existing machinery to fill bigger molds or to manufacture thinner wall parts, in many cases with reduced scrap rates owing to better mold-fill characteristics. The new grades are therefore finding application in a number of areas such as thin wall containers, medical ware, closures, cassettes and others.

The above economic advantages are supplemented in these products by improved property balance since the technologies frequently used to attain high flow can also give rise to narrower molecular weight distributions. Selected properties are compared for polypropylene and high density polyethylene grades in slide 10. It will be appreciated that the high flow narrow molecular weight products have retained or improved on the properties of lower flow broader molecular weight products. It is of particular significance for the applications referred to that impact properties are at least retained since, in general, the trend is to reduced impact (increased brittleness) as the melt flow increases with a particular type of polymer. Similarly, stiffness (flexural modulus) and strength properties are retained or improved so that a better overall balance of properties can be designed into the finished part.

Solid Phase and Thermoforming

Supplementing the introduction of new high flow polyolefins in injection molding, new conversion processes are also being developed for thin walled parts. Prominent among these currently are the solid phase forming processes which include stamping (automotive fender liners, deck floors), forging (gears, wheels) and solid phase pressure and stretch forming (food containers, cans, jars, etc.). The factors favoring

solid phase forming as exemplified by the Shell Solid Phase Pressure Forming or the Dow Scrapless Forming Processes⁶) are shown on Slide 11. Processing below the melting point of the polyolefin results in shorter cycle times by reducing the problems associated with the low melt strength and poor thermal properties of polyolefins. The orientation so induced gives tougher parts and enhanced clarity while also allowing the flexibility of forming thick sections if desired. The inherent low forming pressures required (ca. 100 psi) also allow the use of lower cost tooling compared to injection molding at similar part sizes.

A typical layout is illustrated in Slide 12 for manufacture of juice cups from polypropylene using an Illig pressure former from West Germany. Such a process recently became a reality in the U.S. following earlier precedents in Europe, Brazil, Japan and elsewhere. Further machine development is also in progress to improve the productivity of the current system. The comparative properties and economics of 8 oz. margarine tubs made by this process and by alternative routes are compared in slide 13.

It is also of interest that new grades of thermoformable polyolefins are being introduced to increase the adaptability of these materials to existing thermoforming and stamping capacity. The automotive industry is particularly interested in modifying existing metal stamping machinery to manufacture large parts such as fender liners from polypropylene copolymers.

Polyolefin Films

All the major polyolefins are currently used in film applications (Slide 14), although this market continues to be dominated by LDPE (ca. 90% of total polyolefin usage).⁷) Trends in polyolefin film technology concern both resin and machinery developments; the lower volume polyolefins continue to gain increased acceptance in particular market segments as economic conversion processes are developed for resins which retain their characteristic performance advantages. The blown film processes in general require resins of lower flow for good bubble formation and melt strength, while the cast process uses higher flow products to produce films with excellent optical properties, and moderate film strength at high outputs. Film properties in each family of polyethylenes are largely determined by crystallinity (as measured by density). Increases in crystallinity result in increased stiffness, resistance to permeation by gases and oils, tensile strength, and maximum use temperature; on the other hand reduced impact strength, tear propagation, surface gloss, and slower heat sealing rates also follow. Polypropylene and polybutylene are available in only a single density modification, although a degree of control over crystallinity and such properties as optics, toughness, and heat seal characteristics is attained by copolymerization.

One of the main current trends in this area is the replacement of paper (merchandise bags, glassine) by HDPE due to its stiffness and paper-like feel. Longer term, with further improvement in relative economics, the enormous grocery sack market may also become vulnerable. Current trends in HDPE are to lower melt index, lower density and broader molecular weight distribution in order to improve processability while enhancing important properties such as impact and tensile strength and reducing spittiness. This is a delicate balancing act since lower density reduces stiffness and the resultant products tend toward the upper limit of conventional LDPE properties.

On the machinery side, developments are in progress to improve the processing of LDPE by internal bubble cooling. This allows increased output, improved lay flat width gauge control at some increase in equipment costs and required operator skill level. Developments are also in progress to adapt existing process equipment primarily adapted to LDPE to the properties of HDPE such as higher viscosity, higher processing temperature, sharper frost line and increased sensitivity to hot spots and hangups. Guidelines are being developed for improved design of extruder screws, dies, air-rings and bubble configuration.

The manufacture of polypropylene film, although currently of relatively low volume, is characterized by a variety of processes each of which produces products for particular market segments (Slide 15). Product and process development is most intense in oriented polypropylene owing to the product performance advantages such as excellent water vapor barrier properties, good low temperature property retention, and attractive economics over cellophane in such uses as food and cigarette packaging. Process problems remain, owing to the lower stiffness and higher and narrower heat seal range of OPP. These deficiencies are being remedied by machinery modifications, and the development of coatings or modified resins. The versatility of oriented polypropylene to be tailored for applications in shrink and capacitor film in replacement of corrugated and specialty papers lead to expectations of continued high growth.

The processes producing non-oriented film (cast and tubular water quench processes) yield materials of sparkling clarity, high gloss, low haze and stiffness and reduced strength properties compared to OPP. These products, however, compete favorably with LDPE in those apparel overwrap and food packaging applications requiring crispness and clarity. The water quench process is of course well known in Europe and elsewhere and, owing to its inherently low capital investment, allows the entry of smaller firms into a business which, to date, has been heavily capital intensive and largely captive to major producers.

Polybutylene is a relative newcomer to this sophisticated technology of film manufacture, but brings an extremely attractive balance of properties, particularly strength properties such as tear, impact and puncture resistance in each case being superior to the other polyolefins (Slide 16). Polybutylene, however, is more difficult than LDPE to process and heat seal on conventional equipment. This, plus the current high resin cost limits its current use to specialty applications where the superior performance is appreciated such as bulk shipping containers, pipe wrap and hot fill applications. Longer term, as the required process technology develops and raw material and resin costs become more favorable, the penetration of polybutylene into the film market is expected to accelerate.

Polyolefins in Pipe

A variety of plastics are currently used in the more than two billion pound U.S. market for pipe resins. The major polyolefin is high (and medium density) polyethylene for agricultural drainage and irrigation, and gas and water pressure pipe applications.

New pipe systems have recently been introduced with a 720 psi design stress rating which exceed the standard 630 psi rating stipulated for PE by PPI. A new resin has recently been announced by Phillips which meets 800 psi PPI rating. These improved products plus the already established advantages of polyethylene of light weight, corrosion resistance, flexibility and ease of joining by on-site thermo-fusion should increase its penetration into water and gas pipe applications.

Although large diameter pipe (greater than six inches) is currently a low volume polyolefin usage, major growth potential is foreseen. Recently, merchant availability of resin has increased and increased usage is expected for polyethylenes (sewer, industrial, potable water) and polybutylene (industrial, slurry abrasion, mine tailings). The latter resin has the potential to extend the use temperature and pressure range of polyethylene. The abrasion and creep resistance of polybutylene (Slide 17) make it particularly suitable for the more demanding of these applications.

In hot water markets in the U.S., polyethylene is not a contender and the primary plastic materials are polybutylene and chlorinated polyvinylchloride (CPVC) both of which carry a design stress basis of 500 psi at 180°F (83°C). The latter resin however suffers from processing difficulties. The competitive situation in Europe (Slide 18) is somewhat different in that polypropylene copolymer and crosslinked polyethylene also participate. Polypropylene has only limited use in the U.S. in chemical drain lines, although recently it has been introduced into large diameter non-pressure applications.

In processing, the main recent development has been applied to ABS or PVC pipe construction in which weight (and cost) reduction is achieved by coextrusion, both solid/solid and around a foamed core. Polyolefin technology may need to respond in order to retain low pressure price sensitive uses. Spiral wound polyethylene piping is now being introduced for very large diameter pipe (up to 10 ft.) replacing corrugated steel and concrete in culverts and drainage.

Specialty Polyolefins

Among the specialty polyolefins are ultrahigh molecular weight polyethylene and poly(4-methyl pentene-1). UHMWPE has high abrasion resistance (Slide 17), low coefficient of friction, self-lubrication and good chemical, fatigue and impact resistance. Limited processability has hindered broad application although some injection molded parts for gears, machinery components and prosthetic implants are currently being made. Its high resistance to erosion-corrosion make it particularly suitable for materials handling equipment in a wide variety of aggressive environments.

Poly (4-methyl pentene-1), "TPX", is being marketed in the U.S. by Mitsui Petrochemical Industries for applications requiring clarity, heat and chemical resistance and good electrical properties. Its specific gravity (0.83) helps to offset the high cost and it is being used in laboratory and medical ware, electrical applications in microwave equipment, coaxial cable and wire covering.

Summary

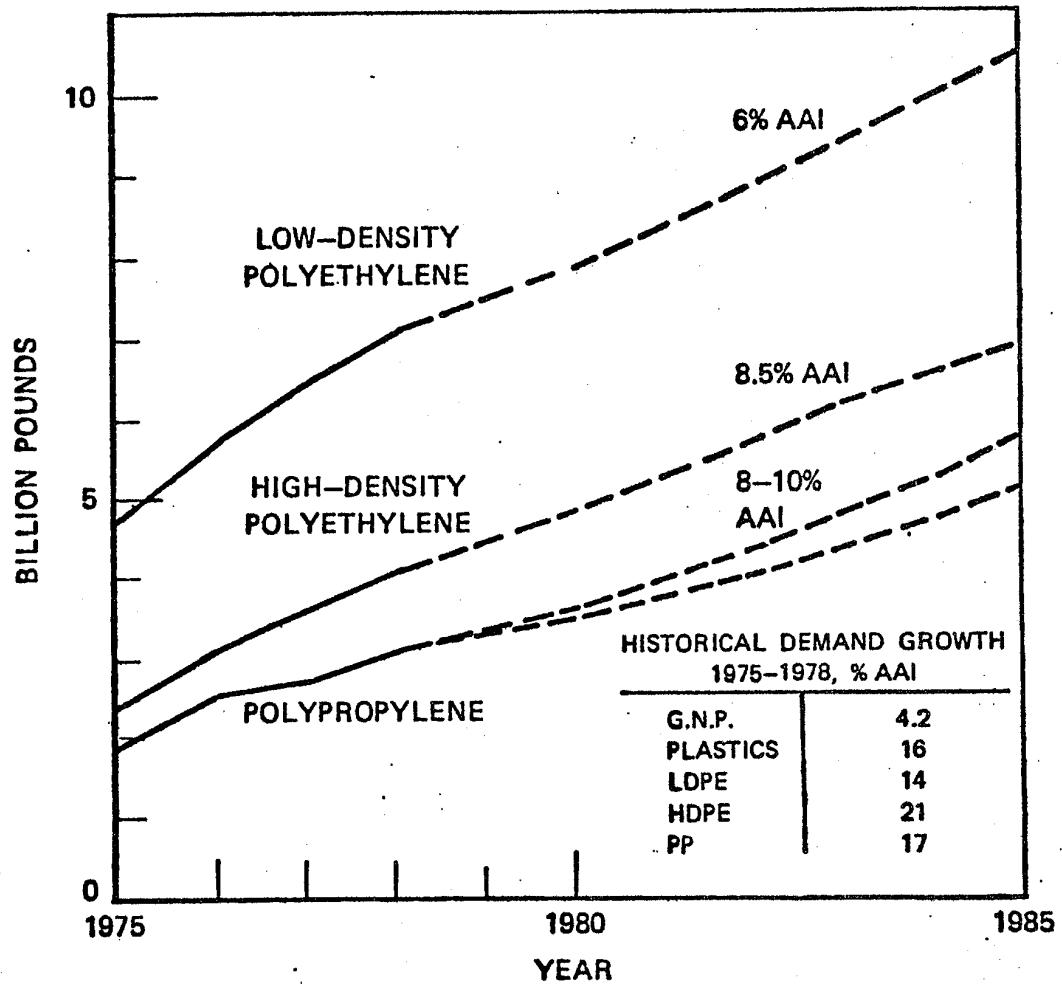
In this paper I have been able to touch on only some of the highlights of recent trends in the U.S. I hope to have illustrated that continuing developments and discoveries in polyolefin technology continue to provide the driving force for the vigorous expansion of these versatile materials into increasingly broader uses and applications.

In closing, I would like to acknowledge with sincere appreciation the expert assistance of my colleagues in Shell Oil and Shell Development Companies in the preparation of this paper.

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4. British Patent No. 1,291,068-9; U. S. Patent No. 3,953,414; L. Luciani, P. C. Barbe', T. Simonazzi, ACS Centennial meeting April 3-9, 1976. Symposium on "New Processes and Technology of the Overseas Chemical Industries".
5. Modern Plastics, January, 1979, page 75.
6. P. M. Coffman, Society of Plastics Engineers, 35th ANTEC, Montreal, April 1977; "Solid Phase Forming as a Production Method", Plastics Institute National Technical Conference, Paper No. 11, Brighton, England, April 1970.
7. Inter-relationships of Polyolefins in the U. S. Film Markets. C. E. Roth, J. J. Pette and P. D. Laudadio, RETEC Polyolefins II, Society of Plastics Engineers, February 14, 1978, Houston, Texas.

U.S. POLYOLEFINS DEMAND GROWTH



02793

FACTORS AFFECTING THE GROWTH OF POLYOLEFINS IN THE U.S.

- * CRACKING OF HEAVY LIQUIDS
- * NON-LEADED GASOLINE
- * ENERGY ECONOMICS
- * ENVIRONMENTAL FACTORS

TECHNICAL FACTORS

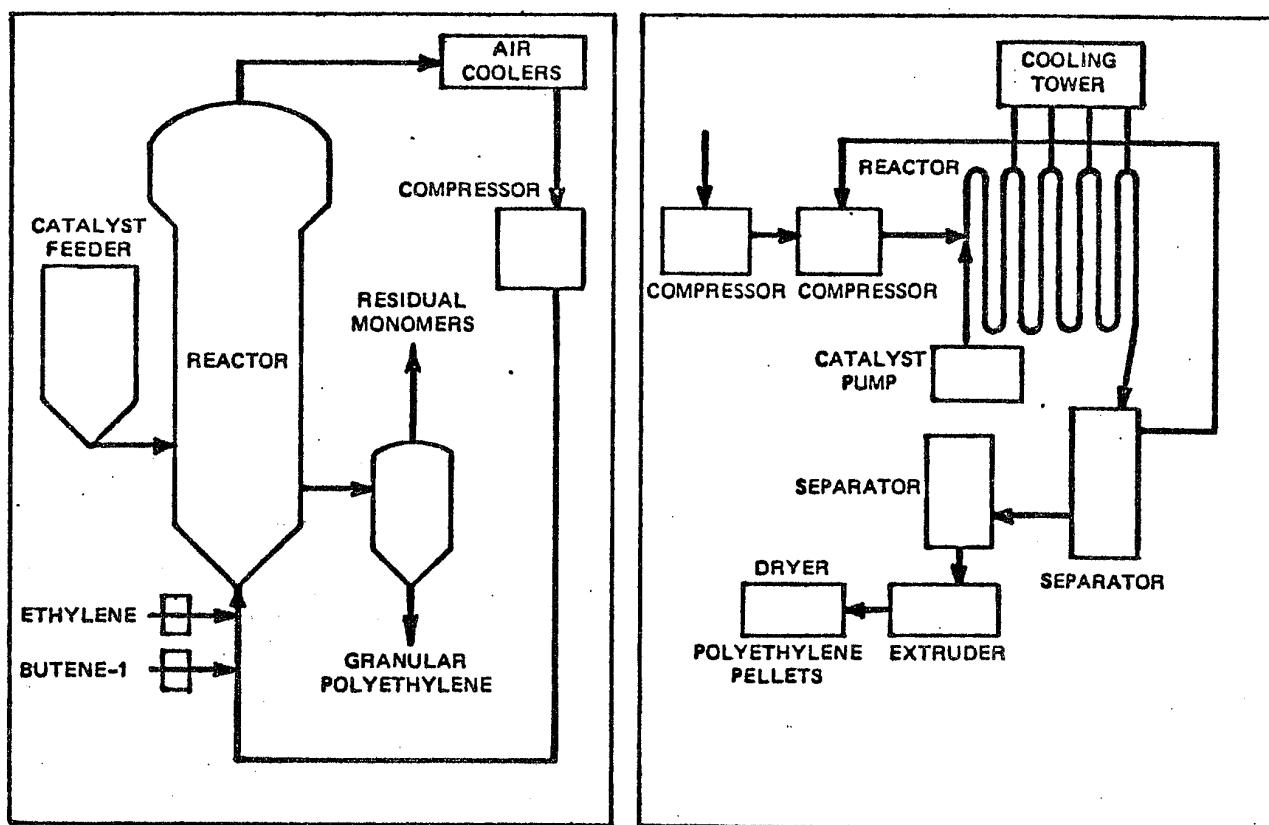
- * MANUFACTURING TECHNOLOGY
- * NEW PRODUCTS AND APPLICATIONS
- * NEW AND IMPROVED PROCESSING OF POLYOLEFINS

COMPARISON OF

GAS-PHASE POLYETHYLENE PROCESS

AND

CONVENTIONAL HIGH-PRESSURE PROCESS



300	OPERATING PRESSURE, psi	30,000-50,000
100	TEMPERATURE, °C	300
2000	COMPRESSOR, HP	11,000
0.5	RELATIVE CAPITAL COST	1
SIMPLE	RECOVERY SYSTEM	COMPLEX
CATALYST	PRODUCT CONTROL	PRODUCTION RATE
MONOMERS		INITIATION
"MINIMAL"	ENVIRONMENTAL FACTORS	REACTOR CONFIGURATION
		HEAT
		NOISE
		WASTE STREAMS

LINEAR LOW DENSITY VERSUS LOW DENSITY POLYETHYLENE

PRODUCT PERFORMANCE COMPARISON

- * HIGHER MELTING POINT
- * STIFFER
- * IMPROVED STRESS CRACK RESISTANCE
- * TOUGHER AT LOW TEMPERATURE
- * INCREASED MELT FRACTURE AT HIGH SHEAR
- * DENSITY RANGE 0.93 - 0.94

CURRENT PRODUCTS TARGETED FOR:

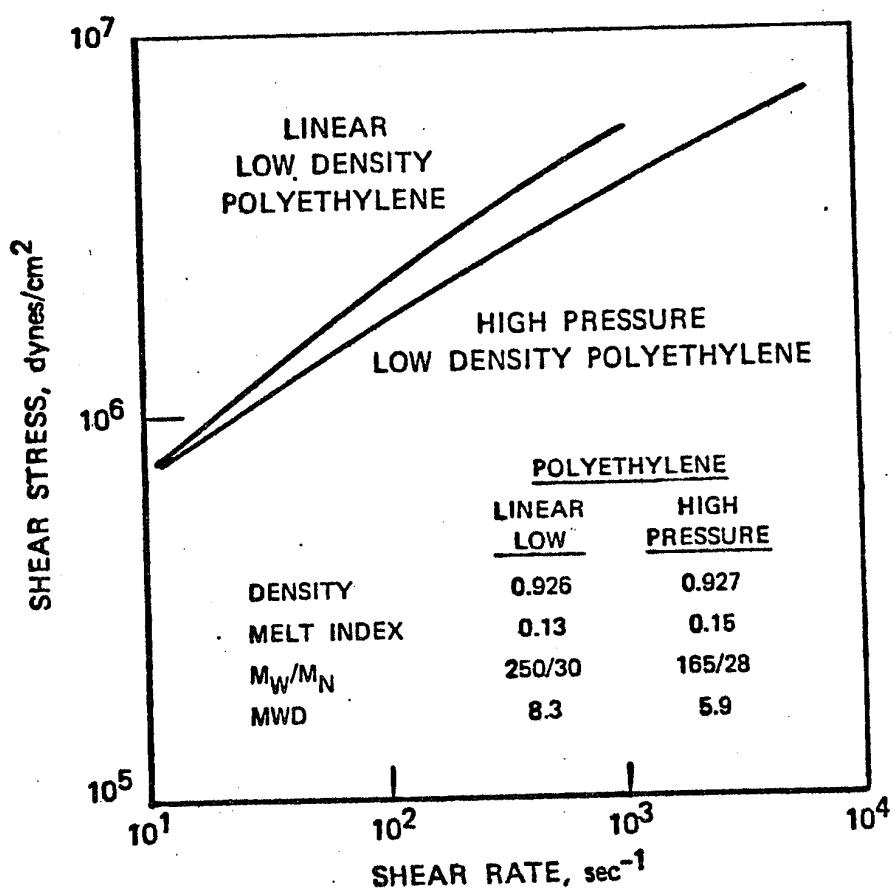
WIRE AND CABLE

INJECTION MOLDING

BLOW MOLDING

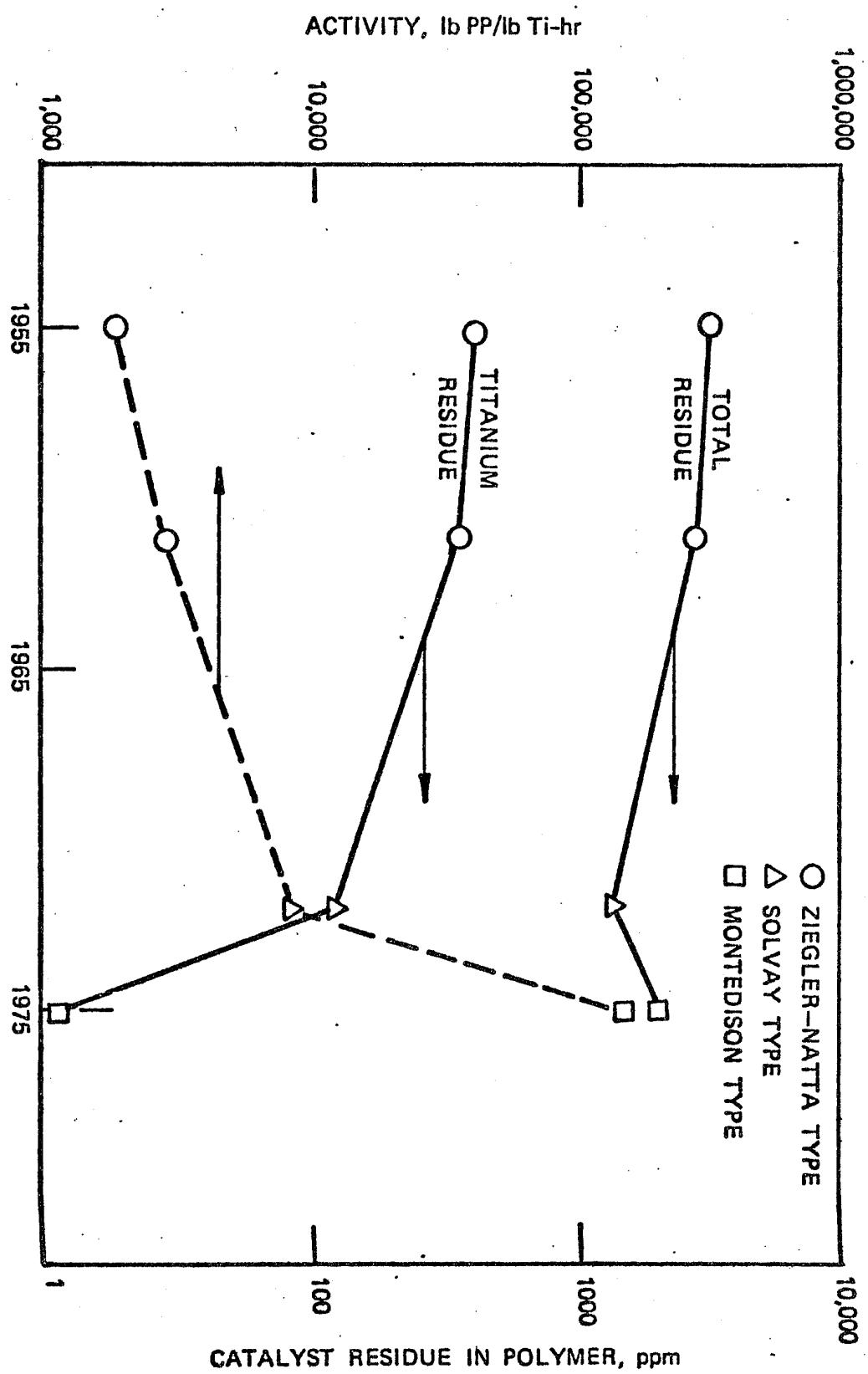
PIPE AND CONDUIT

FLOW STABILITY OF POLYETHYLENES
[C.T. LEVETT ET AL, SPE JOURNAL, 26, 40 (JUNE 1970)]



02793

CHRONOLOGY OF POLYPROPYLENE CATALYST DEVELOPMENT



POLYPROPYLENE CATALYSTS - COMPARATIVE BEHAVIOR

TYPE OF CATALYST

	<u>ZIEGLER-NATTA</u>	<u>SOLVAY</u>	<u>MONTEDISON</u>
--	----------------------	---------------	-------------------

ACTIVITY

LB PP/LB Ti/HR	2,800	8,100	150,000
LB PP/LB CATALYST/HR	250	440	1,075

SELECTIVITY

XYLENE SOLUBLES, %W	6-8	4-6	3-6
---------------------	-----	-----	-----

MORPHOLOGY - CATALYST

AVERAGE PARTICLE SIZE,	15	25	20-25
PARTICLE SIZE DISTRIBUTION	NARROW	NARROW	BROAD

MORPHOLOGY - POLYMER

BULK DENSITY, G/CC	0.4	0.5	0.4
--------------------	-----	-----	-----

PERFORMANCE FEATURES AND APPLICATIONS OF HIGH FLOW POLYOLEFINS

	POLYPROPYLENE		HIGH DENSITY POLYETHYLENE	
	<u>MOLECULAR WEIGHT</u>	<u>NARROW</u>	<u>MOLECULAR WEIGHT</u>	<u>NARROW</u>
	<u>BROAD</u>	<u>BROAD</u>	<u>BROAD</u>	<u>BROAD</u>
MELT FLOW (OR INDEX)	30	12	28	8
TENSILE YIELD STRENGTH, PSI	5,100	4,800	4,500	4,500
TENSILE YIELD ELONGATION, %	8	10	25-1)	1,000-1)
FLEXURAL MODULUS, PSI	220,000	200,000	147,000	140,000
IZOD IMPACT, FT-LB/IN	0.43	0.39	-	-

1) AT BREAK

APPLICATIONS

CLOSURES

CONTAINERS

CASSETTES

MEDICAL WARE

DRAWERS

TOYS

BENEFITS

FASTER CYCLES

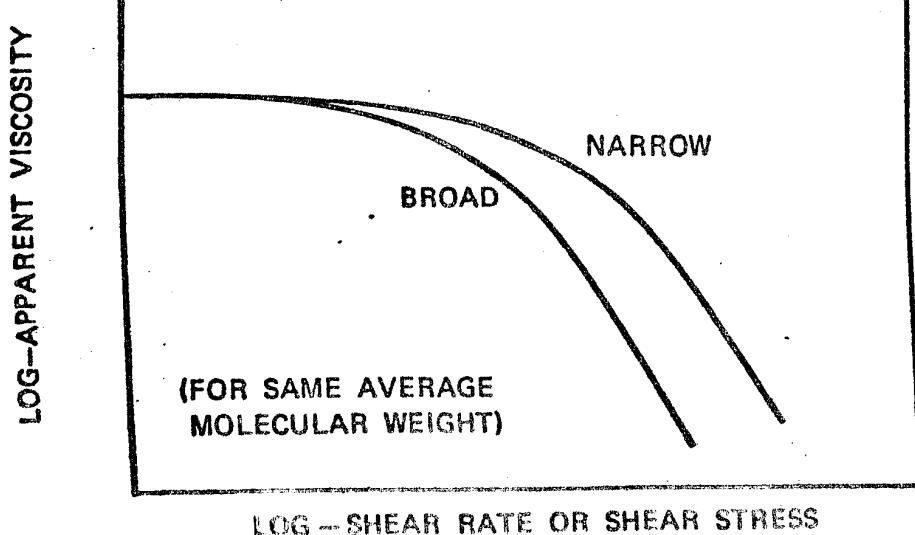
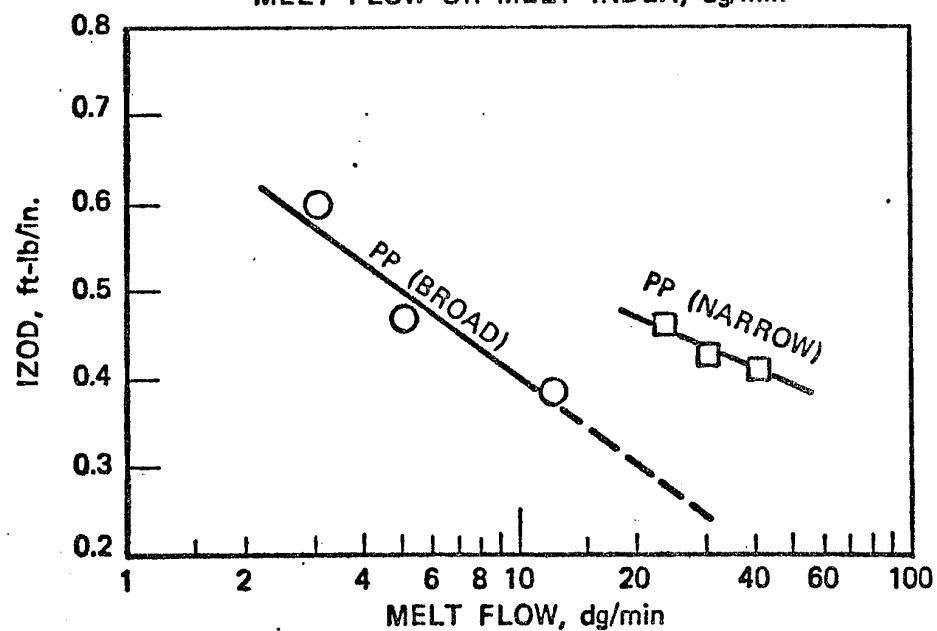
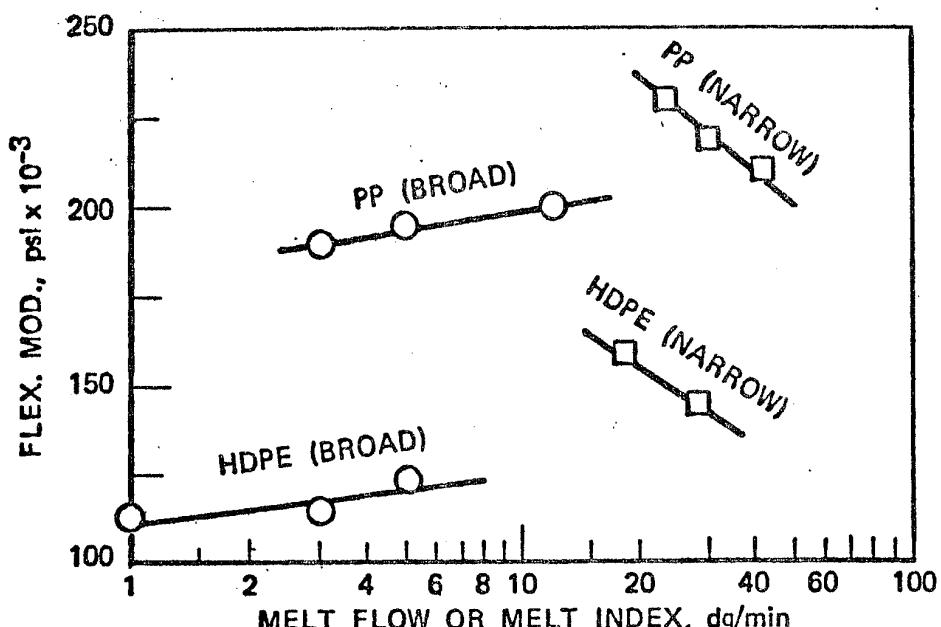
THINNER WALLS

LOWER PROCESSING TEMPERATURE

REDUCED SCRAP RATES

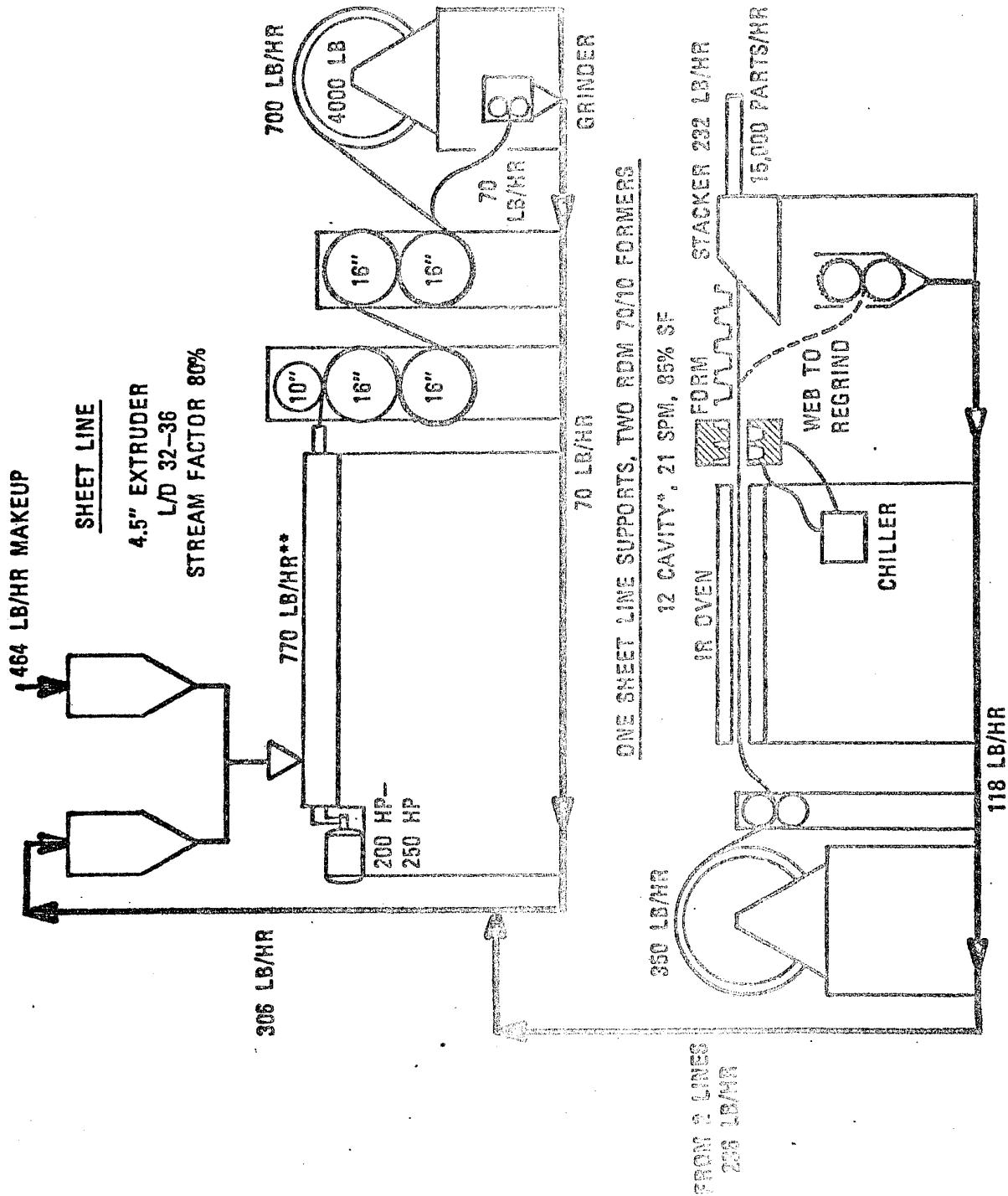
INCREASED PRODUCTIVITY

EFFECT OF MOLECULAR WEIGHT DISTRIBUTION ON
PROPERTIES OF POLYOLEFINS



ADVANTAGES OF SOLID PHASE FORMING

- * FORMING SPEED
- * TOUGH PARTS
- * INCREASED CLARITY
- * THICKER SECTIONS
- * LOW COST TOOLS



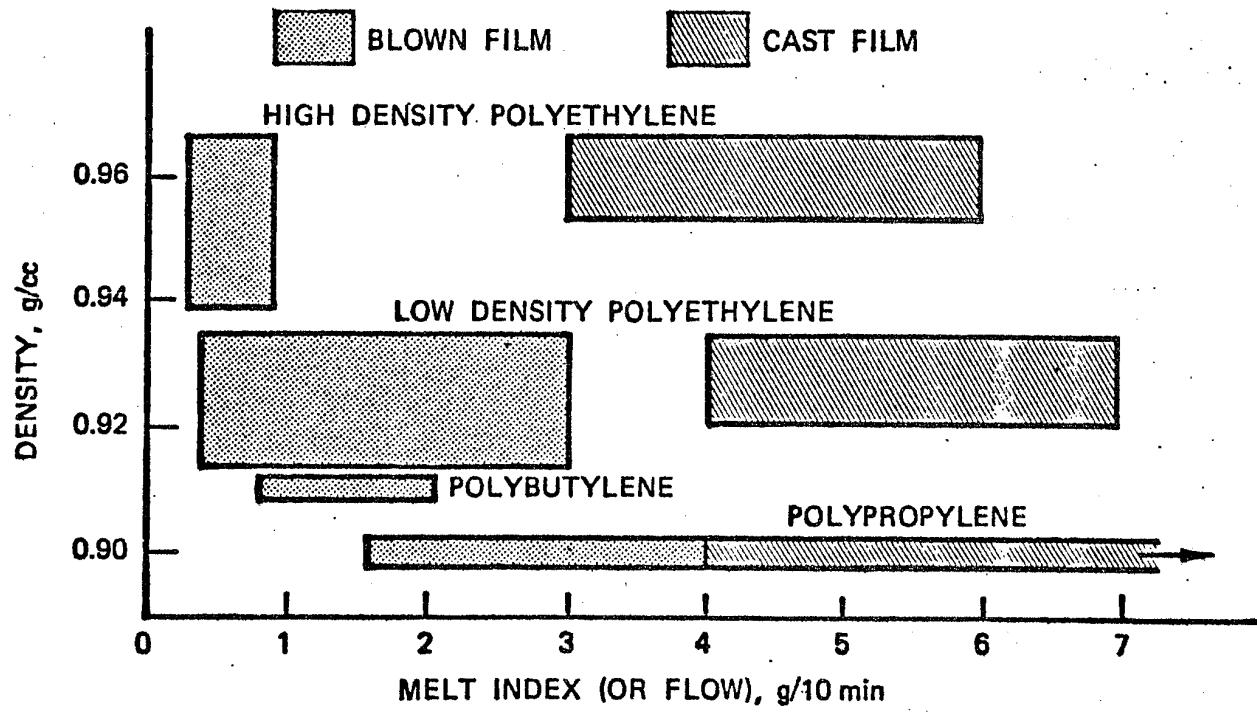
e 14 CAVITY DEMONSTRATED WITH STAGGER PATTERN. MORE DIFFICULT TO OPERATE.
e BELIEVE 900 IS ACHIEVABLE

09825

COMPARATIVE PERFORMANCE AND ECONOMICS OF
8 OZ MARGARINE TUB MANUFACTURE

	<u>SOLID PHASE FORMING</u>	<u>IN-LINE THERMOFORMING</u>	<u>INJECTION MOLDING</u>
MATERIAL	PP HOMOPOLYMER	PP COPOLYMER	ABS
FLEXURAL MODULUS, M PSJ	200-500	150-450	350
IMPACT, -10°F	POOR	EXCELLENT	EXCELLENT
CLARITY	GOOD	GOOD	OPAQUE
STRESS CRACK RESISTANCE	EXCELLENT	EXCELLENT	EXCELLENT
CONTAINER WT. G.	7.0	8.0	9.0
COSTS, \$/1000 TUBS			
MATERIAL	4.6	5.6	10.8
SHEET CONVERSION	1.7	1.9	1.9
FORMING	2.9	2.9	1.2
TOTAL	9.2	10.6	13.9
			15.7

POLYOLEFIN FILM RESINS AND PROCESSES

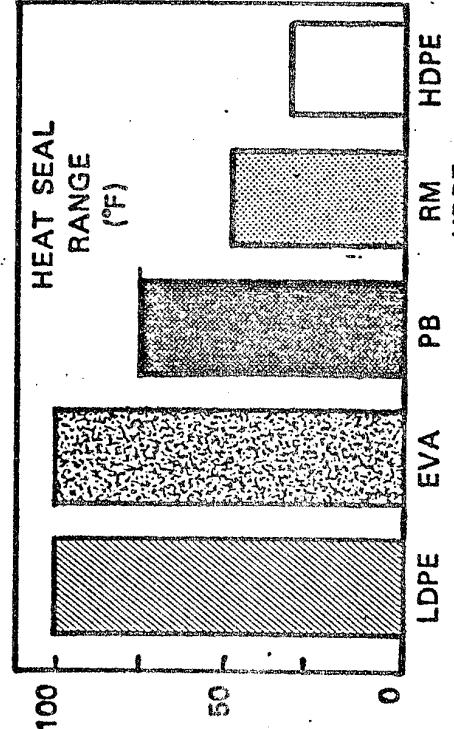
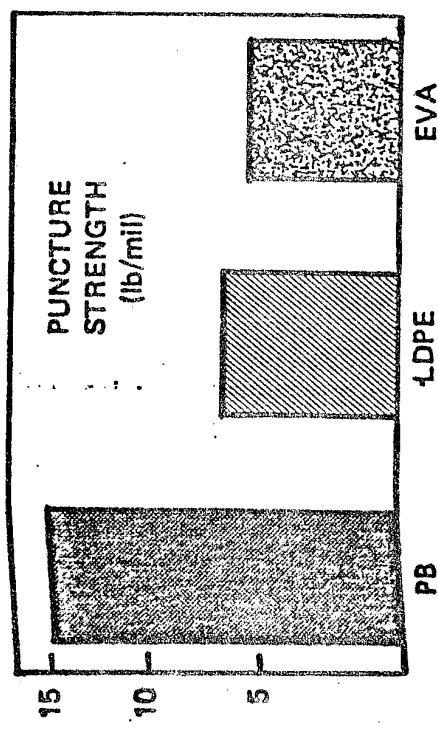
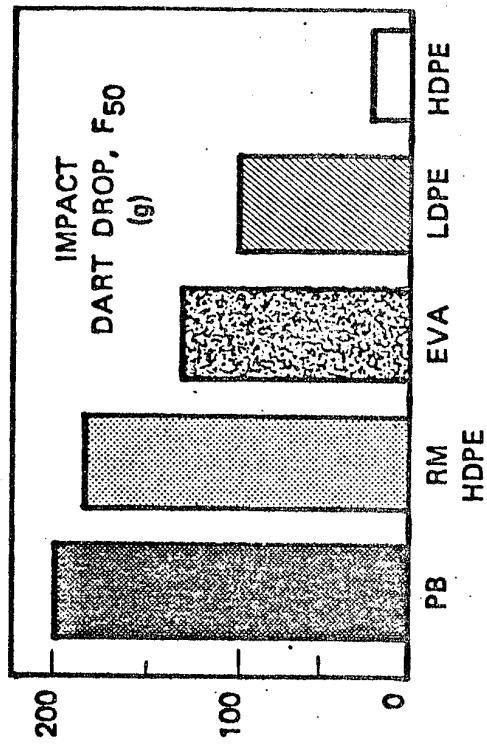
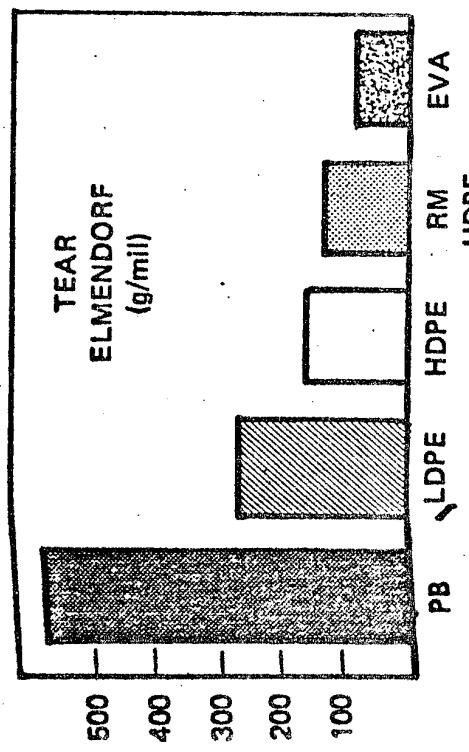


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COMPARISON OF POLYPROPYLENE FILM PROCESSES

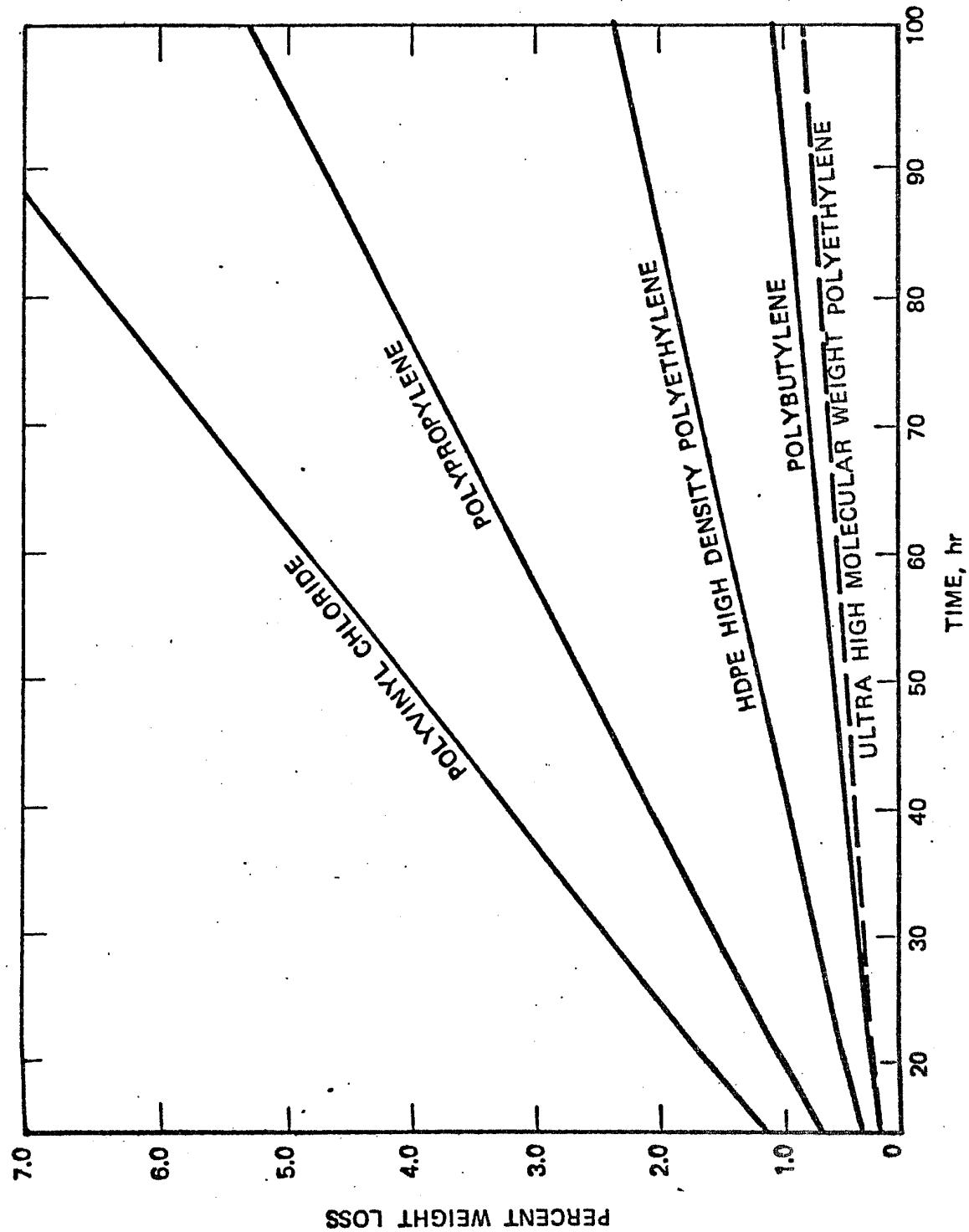
	DOUBLE BUBBLE	TENTER FRAME	WATER QUENCH	CAST
FILM TYPE	BIAXIALLY ORIENTED		UNORIENTED	
TENSILE STRENGTH, PSI	10,000 - 30,000		3,000 - 6,000	
TEAR STRENGTH, ELMENDORF, G/MIL.	4 - 6		40 - 300	
HEAT-SEAL RANGE, °F	REQUIRES COATING		325 - 400	
OPTICAL PROPS	EXCELLENT		GOOD	
RELATIVE CONVERSION COST	HIGH	VERY HIGH	HIGH	LOW
APPLICATIONS	SHRINK FILM	HEAT SET FILM	OVERWRAP	
	FOOD PACKAGING		CLOTHES PACKAGING	
	CAPACITOR FILM	CIGARETTE WRAP		

BLOWN POLYOLEFIN FILM - TYPICAL PROPERTIES



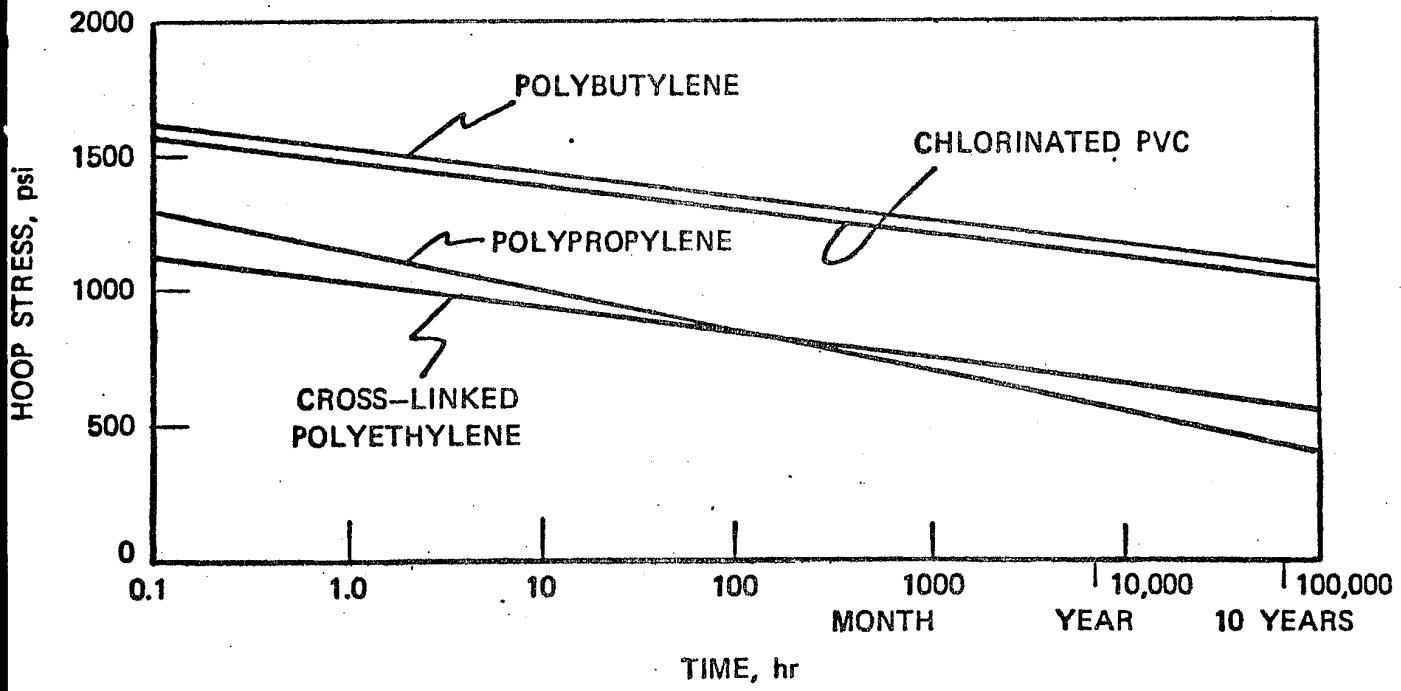
02783

RESISTANCE OF PIPE COMPOUNDS TO SAND SLURRY ABRASION (AT 73°F)



02793

COMPARATIVE PERFORMANCE OF PIPE RESINS
LONG TERM HOOP STRESS RESISTANCE - 180°F



SOCIETY of PLASTICS ENGINEERS

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Gent, June 14-15, 1979

RECENT DEVELOPMENTS IN
MEDIUM VOLTAGE AND HIGH
VOLTAGE POWER CABLE
INSULATION COMPOUNDS

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Dr Alfred CAMPUS
BP CHEMICALS (SUISSE) S.A.
Chemicals and Plastics Laboratory
CH 1217 MEYRIN, Geneva

RECENT DEVELOPMENTS IN MEDIUM VOLTAGE AND HIGH
VOLTAGE POWER CABLE INSULATION COMPOUNDS

Dr Alfred Campus, BP CHEMICALS (SUISSE) S.A.
CHEMICALS AND PLASTICS LABORATORY
1217 MEYRIN, GENEVA

The place of low density polyethylene in the power cable industry

A power cable can be defined as an insulated conductor whose primary function is to transport electrical energy between the source and the consumer. The first power cable made at the end of the 19th Century used oil impregnated paper as insulation material. Because of its good electrical properties it is still used today in various countries, but being essentially an heterogeneous insulation material, requiring hermetic seal and heavy installation, work was initiated to develop the use of homogeneous solid dielectrics. Rubbers and Plastics as a class are inherently electrical insulating materials or dielectrics. Since they also possess many other attributes, such as ease of fabrication and wide choice of physical properties, rubbers and plastics have come to play very early an important role in the insulation of electrical equipment. Called upon to perform a dual function, in that besides providing the required insulation characteristics, a solid dielectric must also serve as a mechanical support for the insulated conductors. The electrical properties alone therefore are not sufficient for the determination of the suitability of a plastic material for a particular application. Due consideration must be given to mechanical, chemical, thermal, water absorption, ageing, weathering and other characteristics. Having set these criteria, the first compound available as solid dielectrics was natural rubber. In the 1940's because of necessity, synthetic rubber (SBR, styrene butadiene rubber) was used, and replaced later by butyl rubber (BR) as improving its operating temperature from 60°C to 80-85°C, temperature approaching that permitted for paper insulated cables. Polyvinylchloride (PVC) was then introduced in the market and found wide application mainly in the low voltage area where the insulating properties are not critical. In the 1950's low density polyethylene (LDPE), which had started as an excellent high frequency insulating material a decade earlier, began to be applied in the medium voltage field. It found immediate acceptance in the power cable industry since its cost was lower than that of existing insulation materials and had much better electrical properties.

From the beginning, however, the temperature deformation characteristics of LDPE was identified as a limiting factor since its maximum cable operating temperature was 75°C. Early in the 1960's a method of upgrading the thermal performance of LDPE was introduced; this included the use of a peroxide to chemically crosslink the insulation. This increased the maximum operating temperature of the cable from 75°C to 90°C, improving in the meantime its mechanical resistance without affecting substantially the electrical properties. Today, vulcanisable polyethylene (XLPE) has captured a great part of the market in the USA and its use is now developing in most countries in Europe, in the medium/high voltage fields.

The wide acceptance of crosslinked polyethylene insulated power cables is due to its unique combination of highly desirable electrical, physical and mechanical properties, some of which are:

Electrical

- High dielectric strength
- High insulation resistance
- Good stability of electrical properties in water
- Low dissipation factor and dielectric constant

Physical (Insulation)

- Excellent ageing in air
- Excellent resistance to sunlight with proper compounding
- Does not melt and flow even at emergency overloads
- Excellent resistance to normal cable environments
- Can be made semiconductive and used as a shield
- Low embrittlement temperature

Mechanical

- High resistance to abrasion, tear and impact
- Easily spliced and terminated
- Can be manufactured in long continuous lengths
- Lightweight

The performance of power cables insulated with LDPE and XLPE

The outstanding properties of LDPE and XLPE insulated power cables have been confirmed on many occasions in long term laboratory ageing tests and actual cable life in service in the electrical distribution system. Recent evaluation in our company of two 11.6/20kV cables, respectively a thermoplastic and a crosslinked version of a construction type widely used in Europe, has confirmed the excellent reputation of this type of insulating compounds. After

5000 hours ageing at three different voltages $U_A = 58\text{kV}$, 65kV and 70kV , under conductor heat cycling for 8 hours at 75°C for the thermoplastic cable and at 90°C for the crosslinked version, followed by 16 hours natural cooling to room temperature, no breakdown has been observed for the various cable samples evaluated.

Over the years the insulation compounds and cable production techniques have been improved to the extent that a substantially reduction of cable failure rate has been reported while the length of installed extruded dielectric cables has increased significantly.

It is generally accepted that over 90% of failures in buried cables are caused by mechanical damages during installation and dig-ins, and for the remaining 10% the cause is unknown and not necessarily electrical.

Recently Bill Thue of Florida Power and Light Co has reported the electrical failure rate for thermoplastic LDPE and XLPE insulated cables over the last 15 years. The data supplied covering about 25% of the total amount of cables manufactured and installed each year in the USA show a trend towards a lower probability of electrical failures for XLPE insulated cables.

Studies initiated in 1970, highlighted the possibility that relatively slow degradation of the insulation layer could be the starting point of an electrical breakdown. This type of damage progresses through the dielectric section under electrical stress, such that, if visible, its path resembles a tree. Although trees can grow in any organic dielectric, much of the work reported in the literature has been done with polyethylene because LDPE has now been identified as the dominant insulating material.

Treeing in solid extruded dielectrics

The literature on treeing composed of hundreds of publications going back to 1912 has been reviewed and reported by R. M. Eichhorn of Union Carbide in 1977. Generally it is accepted that all trees in insulating materials will start at sites of high and divergent electrical stress. Given this precondition, three types of trees can be defined.

An electrical tree is caused by electrical stress alone and is accompanied by measurable partial discharges. This results in a visible and permanent desintegration of the insulation. Most likely they are initiated at imperfections in the cable insulation such as voids, protusion from a shield, contaminants including metal particles and fully oxidised particles or carbon.

A water tree, more diffused in appearances does not show a major trunk as the electrical tree and does not consist of permanent hollow channels formed by the destruction of the material; in these conditions no partial discharges are detected. A possible mechanism implies that under a voltage gradient, moisture is penetrating into the insulation around very fine paths resembling a tree, a bush, or a bow tie tree starting at a site of higher electrical stress. When the voltage and the source of water is removed, most of the water diffuses away, evaporates and the tree disappears.

An electrochemical tree similar to a water tree in appearance is caused by the presence of solute ions that move under the action of an electrical field. Such typical trees have been found next to the conductor shield, where solute metal ions originating from the conductor itself have been identified.

Realizing that most cables in service show presence of various types of trees of different sizes, the question arises whether trees are responsible for electrical cable failure. Laboratory experience has shown that the presence of water trees reduces the dielectric strength of the cable to a value still well above the normal operating conditions of the cable. Recent investigation however has shown that the impulse strength of cables loaded with water trees can be reduced below the protection level provided by the surge arrestors; this seems today to be the only case where a cable could fail because of the presence of water trees,

Unfortunately after electrical breakdown of the cable, it becomes impossible to identify the reason of the failure due to physical destruction of the evidence.

To date, no one has really established a good correlation between the presence of trees in the cable and its probability of failure. It is certainly true that many cables in service do have trees but continue to perform satisfactorily; nevertheless the presence and the size of such weaknesses in the insulation, starting at sites of high divergent electrical stress has now become one of the major discussion subject and concern of the power cable industry.

Ways to minimize the presence of trees

As stated earlier, treeing will initiate in extruded solid dielectrics at sites of high divergent electrical stress; reducing the number of these sites by quality control and improving the cable construction by good protection of the insulation are ways to minimize the presence of trees. Some of the parameters affecting the cable performances are listed in the following table.

<u>VARIABLES</u>	<u>BEST CONDITION</u>	<u>WORST CONDITION</u>
Imperfections	none	protusions, voids, contaminants
Electrical stress water	low none or outside	high water at conductor
Protection	external lead sheath	none
Operating conditions	no surges	high impulses
Materials		
- insulation	feed of clean, uniform controlled compound to the extruder	additives incorporated at the extruder
- Semiconductive shields	dry, smooth surface	rough surface protusions at the interface
Type of cable	extruded shield	taped shield

The critical factors defining a high voltage insulation compound are

- cleanliness
- uniformity in processing and curing characteristics
- electrical integrity allowing higher stress level, minimizing the moisture content creating voids in the insulation.

Another approach now evaluated by various laboratories is the development and the use of so called "Tree Retardant" compounds. Although some of these compounds have already been used for a number of years, recently a great effort has been done to further modify polyethylene to make it even more permanently resistant to tree growth. The testing of these improved compounds is made more difficult by the fact that no generally accepted test is available in the industry to predict the cable life in relation to the treeing phenomenon. The laboratory tests developed for the evaluation of these compounds meet their objectives to the extent that selection of the optimum formulation can be made for further testing on cable samples. These tests, described in the Union Carbide literature are essentially based on the presence of a "Standard defect" in a molded test specimen simulating the effect of a contaminant or insulation

surface roughness in an actual cable construction in that it concentrates the electrical stress and serves as a possible initiation site for a tree growth. Also the standard defects (needles) give a controlled and reproducible stress concentration allowing the comparison of various formulations and the choice of the best candidates for cable testing.

So, tests have been developed for initiating electrical trees and water trees.

Based on these tests, compounds have been developed meeting the following criteria:

- permanence of the tree retardant effect
- safety of the whole formulation
- compatibility of the additives with the base polymer during the whole cable life time.
- extrudability
- normal properties for a high voltage insulation compound such as electrical, chemical, mechanical and high level of cleanliness.

This type of compounds are now being introduced to the power cable industry in the USA as well as in Europe with preliminary good results.

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POLYPROPYLENE STRUCTRURAL FOAM

Patrick A.M. ELLIS

Hercules Chemicals nv

B 3940 Paal-Beringen

POLYPROPYLENE STRUCTURAL FOAM

1. INTRODUCTION

Polypropylene Structural Foam is one of the more recent additions to the family of thermoplastics, which are used in this application. It is characterised by being the lowest cost, lowest density and one of the most versatile members of this group. One of its main advantages is its ability to accept modification by the addition of mineral fillers, such as talc, chalk and mica, as well as reinforcement with glass fibers. Polypropylene resins are currently available in two forms, homopolymers, and copolymers of propylene with ethylene. The former are characterised by having a high level of crystallinity, which gives them a relatively higher stiffness compared with the copolymer versions; the copolymers, on the other hand have higher impact resistance.

Polypropylene Structural Foam is a single operation injection moulded polypropylene sandwich of rigid closed-cell foam encapsulated in a full density skin. The closed cell foam is formed through expansion of a dissolved gas that is uniformly dispersed throughout the polymer melt. Gas introduction and subsequent dispersion can be accomplished either by the preblending of pellets with a suitable blowing agent or by injection of gas into the melt prior to mixing. The resin-gas solution is injected into the closed mould; the gas comes out of solution, forming bubbles and forcing the melt to expand; skins are formed through shearing and cooling at the mould surfaces, and the gas bubbles become closed cells upon cooling. The cells reduce the density of the moulded part and increase the stiffness versus the same weight of solid polymer through an increase of the moment of inertia of its walls.

2. PROPERTIES OF POLYPROPYLENE STRUCTURAL FOAM

Polypropylene Structural Foam has a number of unique properties that makes it especially interesting.

2.1 Low density - Polypropylene produces the lowest density structural foam ($0,55 - 0,70 \text{ g/cm}^3$)

2.2 High stiffness - Polypropylene Structural Foam mouldings have between two to three times the stiffness of unfoamed polypropylene and up to fourteen times the rigidity of the same weight of steel. Naturally, the stiffness of a component is a function of core density and part thickness, but certain simplified formulae can be used to predict part stiffness (1,2).

They are : $\frac{W}{X} = \frac{48EI}{L^3}$ where the load, W on the

centre of the beam gives the deflection X, E being the modulus, I, the moment of inertia of the section and L, the length of the beam. For a load distributed along the full length of the beam, the formula is :

$$\frac{W}{X} = \frac{384 EI}{5L^3}$$

It is not the purpose of this paper to go into detail at this point, but since stiffness is possibly the most important property of Polypropylene Structural Foam, it is worth a small diversion. The modulus of a typical homo-

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92

polymer will be between 0,9 and 1,1 GPa depending on the density and that of a typical copolymer will be 0,70 to 0,85 GPa. Naturally this property may be modified by the addition of mineral fillers as well as glass fibers, but this will be referred to later on in this paper.

As has been already mentioned, the properties of Polypropylene Structural Foam depend on the part thickness and density and Table I illustrates the comparison between a Polypropylene homopolymer and a copolymer at 6,4 mm and 12,8 mm.

- 2.3 High Temperature Resistance - The cellular core of Polypropylene Structural Foam has the effect of improving the heat insulation properties. This coupled with the low thermal conductivity of Polypropylene as well as its inherently good heat resistance makes Polypropylene Structural Foam one of the highest heat resistant low cost structural foams on the market.
- 2.4 Chemical Resistance - Polypropylene Structural Foams have outstandingly good chemical resistance and especially good environmental stress cracking resistance. This makes Polypropylene Structural Foam ideal in certain chemical environments, excluded to Styrenic Structural Foams.
- 2.5 Flexural Cyclic Fatigue Resistance - Unlike other plastics, Polypropylene Structural Foam gets stronger rather than weaker when subjected to vibration or cyclical flexing. In a comparative test carried out recently Polypropylene Structural Foam easily out-performed an ABS Structural Foam (TABLE I).

(3)

TABLE I

COMPARISON OF POLYPROPYLENE WITH ABS STRUCTURAL FOAM

STATIC PROPERTIES	FLEXURAL STRENGTH				FLEXURAL MODULUS				DENSITY g/cc 23° C 0.69
	MPa		23° C	100° C	MPa		23° C	100° C	
ABS FOAM	50.3	4.2			1381	196			
POLYPROPYLENE HOMOPOLYMER	22.0	6.1			665	134			0.48
POLYPROPYLENE COPOLYMER	19.3	5.5			606	154			0.43
CYCLIC PROPERTIES			100° C, 2 CYCLES/HR.						
			FLEXURAL CREEP AND RECOVERY						
	%	%			%	%			%
	STRESS MPa	PEAK STRAIN 20 CYCLES			PEAK STRAIN 140 CYCLES	RESIDUAL STRAIN 20 CYCLES			RESIDUAL STRAIN 140 CYCLES
ABS FOAM	1.0		SPECIMEN DEFLECTED TO LIMIT OF APPARATUS						
	1.7		AFTER 15 MIN. AT ALL STRESS						
	3.4		LEVELS.						
POLYPROPYLENE HOMOPOLYMER	1.0	1.52	1.54		0.71				0.78
	1.7	2.2	2.32		0.79				0.95
	3.4	7.4 (18 cycles)	LIMIT OF APPARATUS - TEST STOPPED						
POLYPROPYLENE COPOLYMER	1.0	1.36	1.40		0.52				0.58
	1.7	2.08	2.11		0.69				0.75
	3.4	8.22 (18 cycles)	LIMIT OF APPARATUS - TEST STOPPED						

2.6 Electrical Properties - Because of the good electrical resistivity and high dielectric strength of polypropylene the structural foam can be used for electrical insulation applications.

2.7 Water and Water Vapour Transmission - Water is essentially insoluble in polypropylene, thus it has very low water or water vapour transmission.

2.8 General Physical and Mechanical Properties - The General Physical and Mechanical Properties of Polypropylene Structural Foam are summarized in Table II.

TABLE II
PHYSICAL AND MECHANICAL PROPERTIES OF POLYPROPYLENE STRUCTURAL FOAM

	HOMOPOLYMER		COPOLYMER			
	Thickness (mm)					
* Data not available						
PROPERTY	6.4	9.5	12.7	6.4		
DENSITY g/cc	.67	.67	.67	.67		
FLEXURAL MODULUS MPa	847	792	765	741		
FLEXURAL STRENGTH MPa	22.0	20.7	17.2	16.9		
TENSILE STRENGTH AT YIELD, MPa	13.1	11.8	9.9	11.7		
ELONGATIONAL YIELD/BREAK %	7/17	6.8/14	6.8/12.8	5.7/18		
SHORE HARDNESS D SCALE	63	63	64	45		
COMPRESSIVE STRENGTH, MPa				45		
PERPENDICULAR TO SKINS	11.0	15.8	22.0	*		
PARALLEL TO SKINS	19.3	23.4	27.6	*		
FLEX. LOAD AT 2.5 % STRAIN KGS.	8.3	*	*	*		
FLEX. LOAD AT 5.0 % STRAIN KGS.	13.2	*	*	*		
POISSONS RATIO AT 23° C		*	*	*		
FLOW DIRECTION	.35	*	.31	*		
ACROSS FLOW	.39	*	.36	*		
POISSONS RATIO AT .60° C		*	*	*		
FLOW DIRECTION	.39	*	.39	*		
ACROSS FLOW	.44	*	.50	*		
DROP WEIGHT IMPACT, J (454 grams)						
23° C	2.3	4.4	6.7	4.8		
- 20° C	1.9	2.6	3.5	1.9		
- 29° C	*	*	*	1.2		
				5.6		
				8.3		
				2.5		
				3.4		
				1.6		
				1.9		

3. THE APPLICATIONS FOR POLYPROPYLENE STRUCTURAL FOAM

- 3.1 Agriculture and Food - For agricultural and food handling uses, Polypropylene is easy to clean and sterilise because of its high temperature corrosion resistance and autoclave sterilizability. Also its low density makes it easy to lift, store, handle and less costly to ship. For farm machinery the corrosion-resistance, fatigue resistance and sound damping properties of Structural Foam Polypropylene are important.
- 3.2 Appliances and Business Machines - Of importance in this applicational area are the rugged durability, good heat resistance (under both wet and dry service conditions), chemical and detergent resistance, high rigidity and impact strength as well of course, good electrical properties of Polypropylene Structural Foam.
- 3.3 Automotive and Batteries - The automotive industry uses Structural Foam Polypropylene because of its light weight, high stiffness (allowing metal replacement) together with good heat resistance, as well as resistance to petrol and oils. The excellent fatigue resistance together with sound deadening properties are also essential. Table III outlines a cost analysis for a Polypropylene Structural Foam boot. The principal dimensions were 46 cm x 102 cm in plan view, while the thickness was 6,4 mm as was the ribbing. The component weighed 5.5 Kgs.

TABLE III

ECONOMIC ANALYSIS OF BOOT LID IN GLASS REINFORCED STRUCTURAL FOAM

<u>COST ITEMS</u>	<u>PER PART</u>
MATERIALS (95 % UTILIZATION)	
POLYMER (COPOLYMER)	4.5 KG AT BF. 30/KG = 135
GLASS	1.1 KG AT BF. 50/KG = 55
TOTAL	190
MOULDING CYCLE 2 MINS	
PARTS/HOUR 80 % of 30 =	24
PARTS/YEAR 365x24x 24 =	210,240.
LABOUR	
BASE PAY	200/HR
OVERHEADS 75 % OF BASE	150/HR
TOTAL/HR	350
TOTAL/PART (24 PARTS/HR) =	14.6/PART 14.6
MOULD	
INITIAL COST	6,000,000
MAINTENANCE 10 %	600,000
TOTAL	6,600,000
AMORIZATION OVER 5 MODEL YEARS	
	1,051,200 PARTS
MOULD COST/PART	= 6.3/PART 6.3
MACHINE	
INITIAL COST	10,000,000
MACHINE UTILIZATION 80 %	
7 DAY WEEK	
3 SHIFT DAY	
MACHINE AMORIZATION 5 YEARS	
COST/YEAR	2,000,000
COST PART	9.5/PART 9.5
UTILITIES 100/HR	4.2 4.2
MISC. COSTS	10.0
TOTAL COST	234.6

3.4 Building and Construction - The building and construction industry demands for Structural Foam Polypropylene can be summarised by high stiffness, light weight, good chemical resistance and, when painted or correctly pigmented (2 - 2,5 % carbon black), good U.V. resistance. Good examples would be interior doors, shutters, concrete moulds, shower stalls, door frames, cement hods, paint brushes and rollers, etc.

3.5 Furniture - Light weight and stiffness are all important here as well as the ability to be treated like wood, such as paintability, nailability etc. Table IV compares Polypropylene Structural Foam with White Pine with regard to their screw and staple retention :

TABLE IV⁽⁴⁾ - SCREW AND STAPLE RETENTION* FOR
POLYPROPYLENE STRUCTURAL FOAM

<u>Material</u>	<u>Specimen Thickness mm</u>	<u>Skin Thickness mm</u>	<u>Density g/cm³</u>	<u>Pull-Out Force Kg.</u>	
				<u>Screw**</u>	<u>Staple⁺</u>
Medium Impact Copolymer Foam	18	1,3	0,53	161	10,4
White Pine			0,37	109	1,4

* Using ASTM D 1037 as a guide.

** No 10 wood screw with 2,3 mm dia pilot hole

+ 12,7 x 7,9 x 1,6 mm staple.

Polypropylene is resistant to most solvents and its smooth impervious monopolar surface characteristics account for the difficulty in applying finishes by conventional coating methods. Several different surface treatments have been developed by industry whereby good adhesion of paints or varnishes is obtained⁽⁵⁾. The wood-like properties of Polypropylene Structural Foam enable it to be used in both visible and non-visible applications.

Chair frames are of course the obvious choice because of the weight saving properties. However, complete cabinets, bed frames etc. may be made up with Polypropylene Structural Foam.

Though not strictly furniture, one recent use for Polypropylene Structural Foam is for coffins, because of its good resistance to earth loading. Picture frames, flower pots, brush blocks, coat hangers may not really be furniture, yet as household items they are again proof that Polypropylene Structural Foam finds a ready market in wood-like applications.

- 3.6 Sport and Recreation - Once again, because of its wood-like properties it is possible to provide an opening for Polypropylene Structural Foam for most "small boat" applications, such as centre boards, rudders, paddles, oar blades, propellers and even small dingies. Picnic furniture is an obvious replacement area as are gunracks, gun stocks, surfboards, skate boards etc.
- 3.7 Industrial Products - Mention has already been made of food handling, but one could also add materials handling in general. Tool boxes as well as tool handles spring to mind as well as machine guards, lawn mower housings, pumps and other gardening equipment.

4. PROCESSING POLYPROPYLENE STRUCTURAL FOAM

While it is not the intention of this paper to enter into detail on the processing of Polypropylene Structural Foam, reference must be made to special aspects of the subject. In Europe low pressure processes are the most common generally using a blowing agent as the source of expansion gas. Between 0,3 - 0,8 % Azodicarbonamide is considered adequate depending on the desired density.

Mould shrinkage is of course a function of choice of polymer, as well as part thickness.

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Table V illustrates this latter point.

TABLE V - POLYPROPYLENE STRUCTURAL FOAM SHRINKAGE

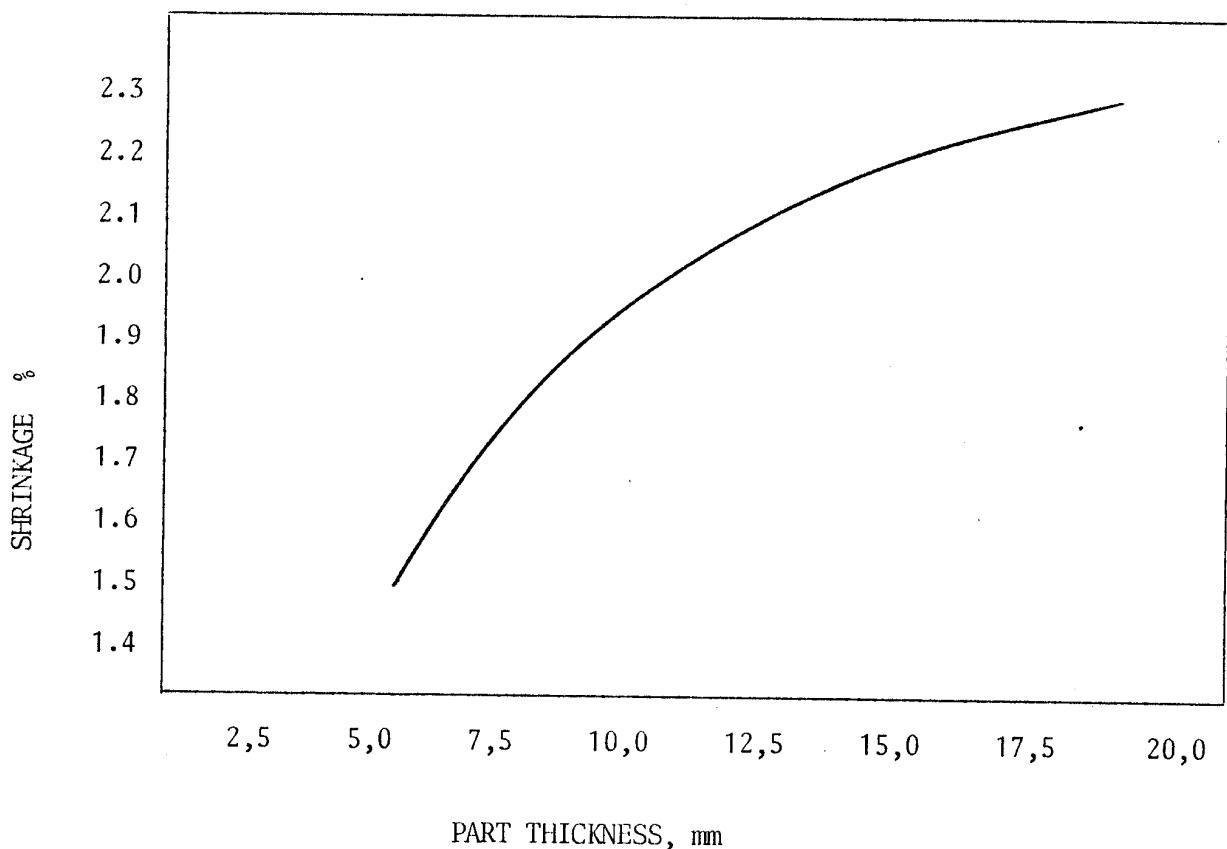
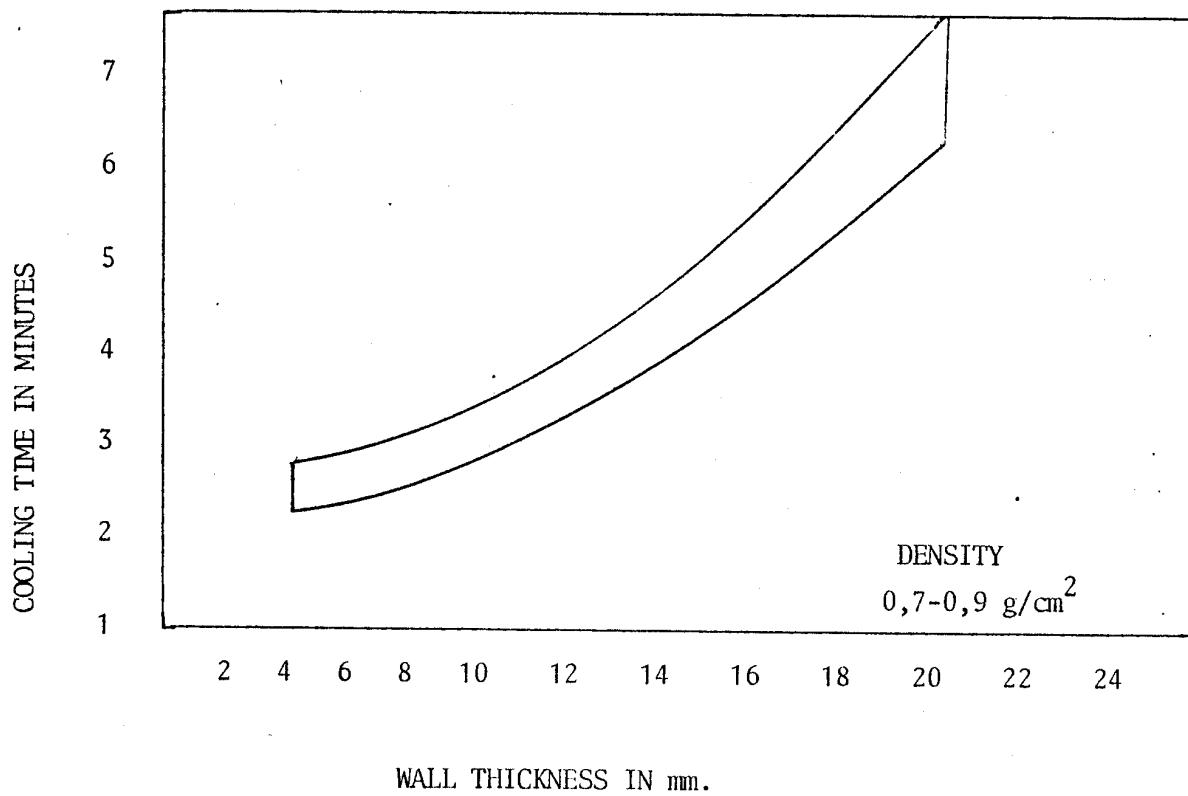


TABLE VI - EFFECT OF WALL THICKNESS ON COOLING TIME

OF STRUCTURAL FOAM POLYPROPYLENE



Part thickness will of course influence cooling time and this is demonstrated in Table VI.

5. MODIFICATION OF POLYPROPYLENE STRUCTURAL FOAM

The properties of Polypropylene Structural Foam can be greatly enhanced by the addition of a filler or reinforcement.

The following Tables (VII, VIII, IX) serve to indicate the interesting extension of the properties of Structural Foam, due to addition of chalk, talc and more recently mica. Modification by the addition of coupled glass fibres has promoted Structural Foam Polypropylene into the sphere of engineering materials. Although Polypropylene burns when ignited, its burning behaviour can be modified by the addition of flame retardant additives. Very soft, flexible foams may also be produced by the addition of up to 40 % EPDM or EP Rubbers. Percentages higher than 40 present flow problems, since one of the most important demand made on Polypropylene is that it have a high flow in order to produce a uniform foam cell struction.

6. CONCLUSION

Despite what has already been said Polypropylene Structural Foam is still in its infancy. The full potential has yet to be realised and hopefully this paper may make some contribution to the fullfillment of this aim.

In closing I would like to acknowledge the help that I have received from my colleagues at Hercules without whose assistance this presentation would not have been possible.

TABLE VII

IMPACT - STIFFNESS
 FILLED HOMO POLYMER
 STRUCTURAL FOAM

<u>FALLING DART IMPACT STRENGTH</u>			
<u>FLEXURAL MODULUS</u>			
	<u>J</u>	<u>-30C</u>	<u>+23C</u>
	GPa	23C	
UNFILLED	0.77	2.3	2.3
15 % TALC	1.18	2.5	2.6
15 % MICA	1.41	2.3	3.4
15 % CHALK	1.05	3.0	3.7
25 % MICA	1.56	2.7	3.4
25 % CHALK	1.12	2.7	4.8
40 % TALC	1.69	1.1	2.2
40 % CHALK	1.30	2.3	4.1

TABLE VIII

STRUCTURAL FOAM		SOLID POLYMER
UNREINFORCED	30 % GLASS REINFORCED	UNREINFORCED
DENSITY, g/cm ³	0.65	0.90
TENSILE STRENGTH, MPa	21.8	23.2
FLEXURAL MODULUS, GPa	0.94	3.05
FLEXURAL STRENGTH, MPa	26.0	52.7
		54.4

TABLE IX

IMPACT STIFFNESS
 FILLED COPOLYMER
 STRUCTURAL FOAM

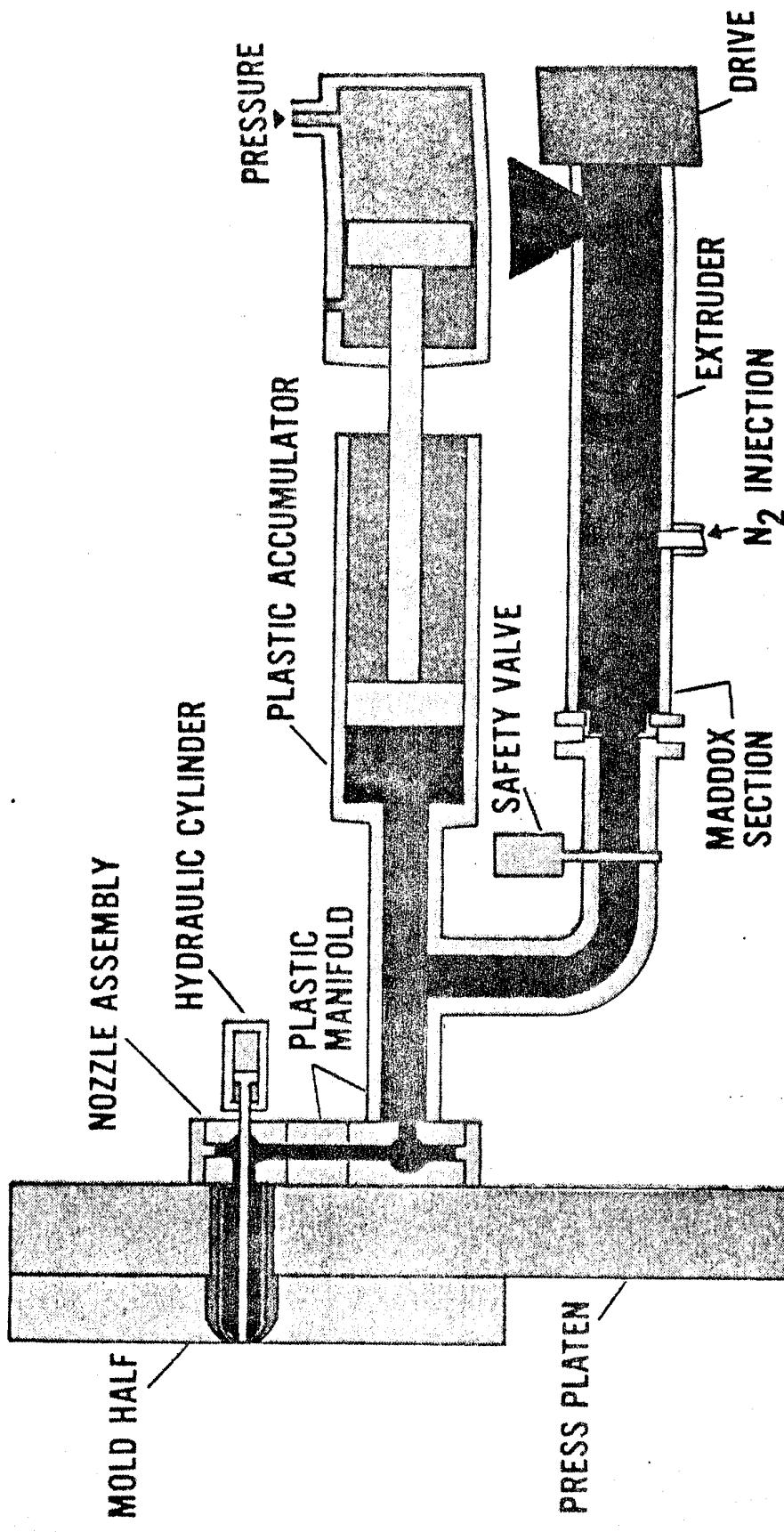
	FALLING DART IMPACT STRENGTH		
	<u>FLEXURAL MODULUS</u>		
	<u>GPa</u>	<u>J.</u>	
	<u>23C</u>	<u>-30C</u>	<u>+23C</u>
UNFILLED	0.70	3.0	7.6
15 % MICA	1.19	3.7	6.5
15 % CHALK	0.91	3.4	7.1
25 % MICA	1.43	3.0	5.4
40 % CHALK	1.12	2.6	7.1

AUTOBIOGRAPHY

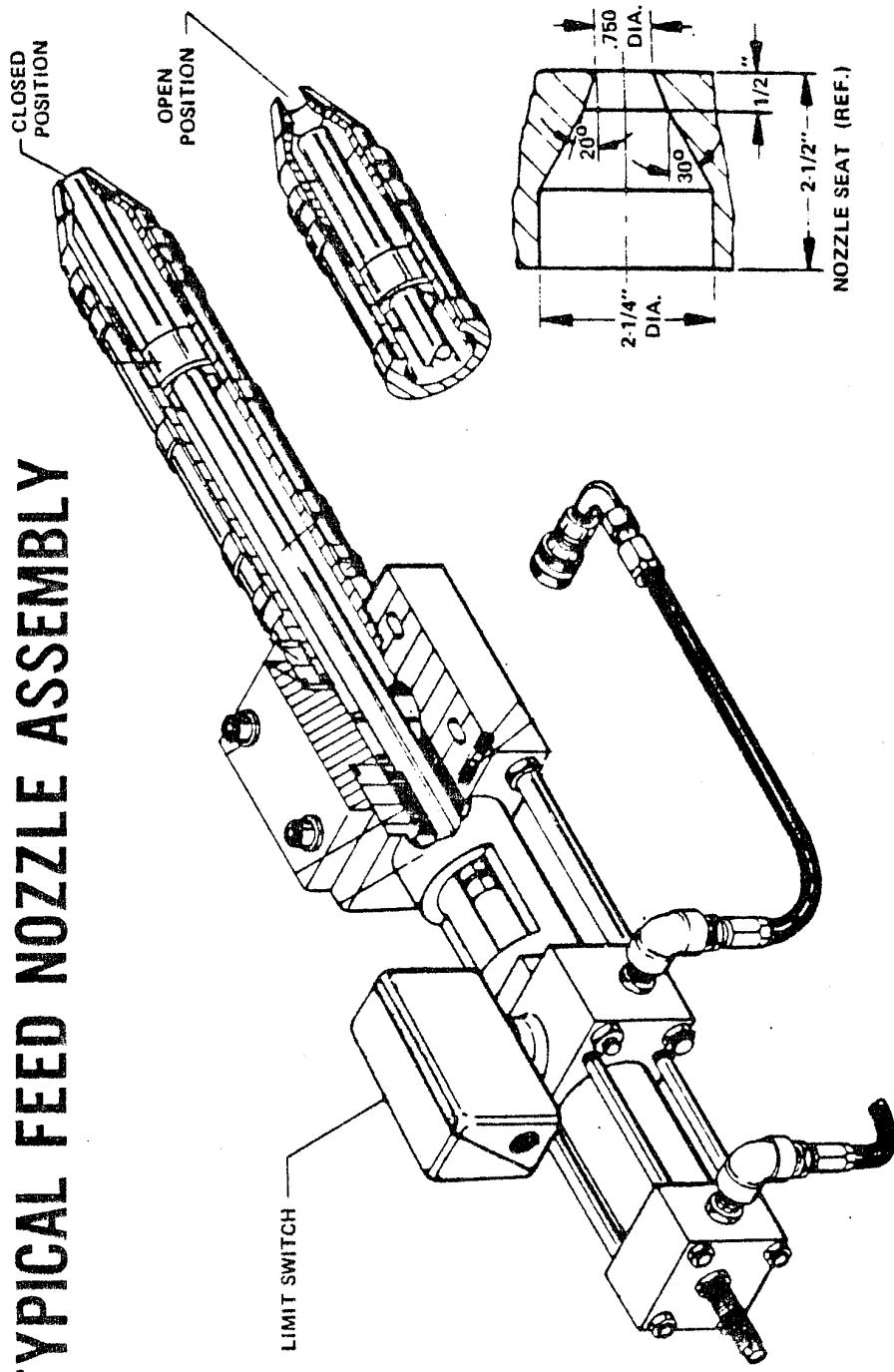
1. The Deformation Behavious of Foamed Thermoplastics by D.R. Moore,
K.H. Couzens, M.J. Iremonger - J. Cellular Plastics Vol. 10 N° 3 1974
2. Simplified Design Procedures for Thermoplastics, by K.V. Gotham,
D.R. Moore, P.C. Powell - Journal Applied Phys. D : Appl. Phys. 1974
Vol. 7
3. Pro-Fax Structural Foam. I - Table II R.H. Heinold - Hercules Incorporated, Polymers Technical Center
4. Polyolefin Structural Foam for Automotive Use by Donal P. Hug and
Charles C. Shockley - National Automobile Engineering Meeting,
Detroit, Mich. May 22-26 1972 (ref. 720475)
5. Wood-Grain Finishes for Pro-Fax Structural Foam. - Technical Information
Report F-166 4/77. Hercules Incorporated Polymers Dept. Wilmington, Del.

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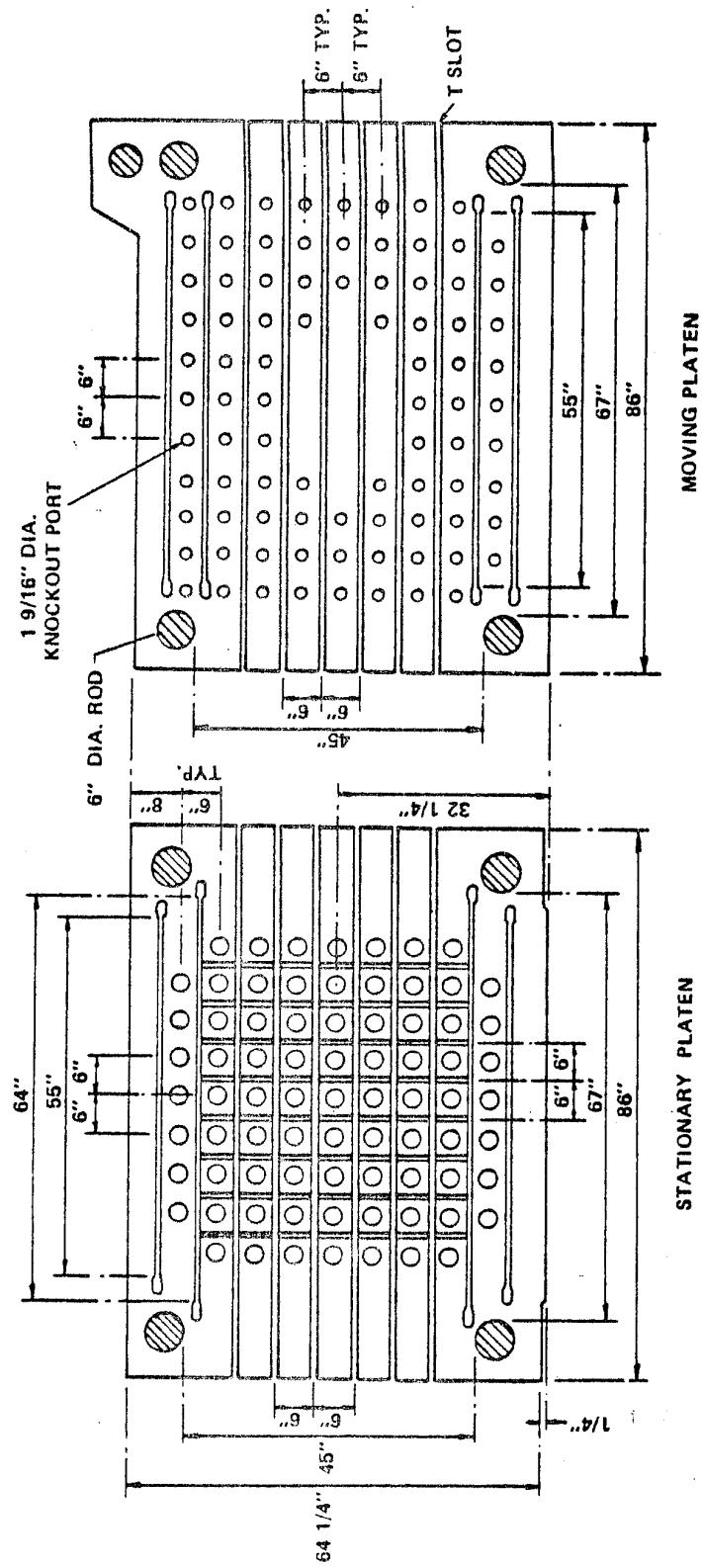
STRUCTURAL FOAM MACHINE SECTION



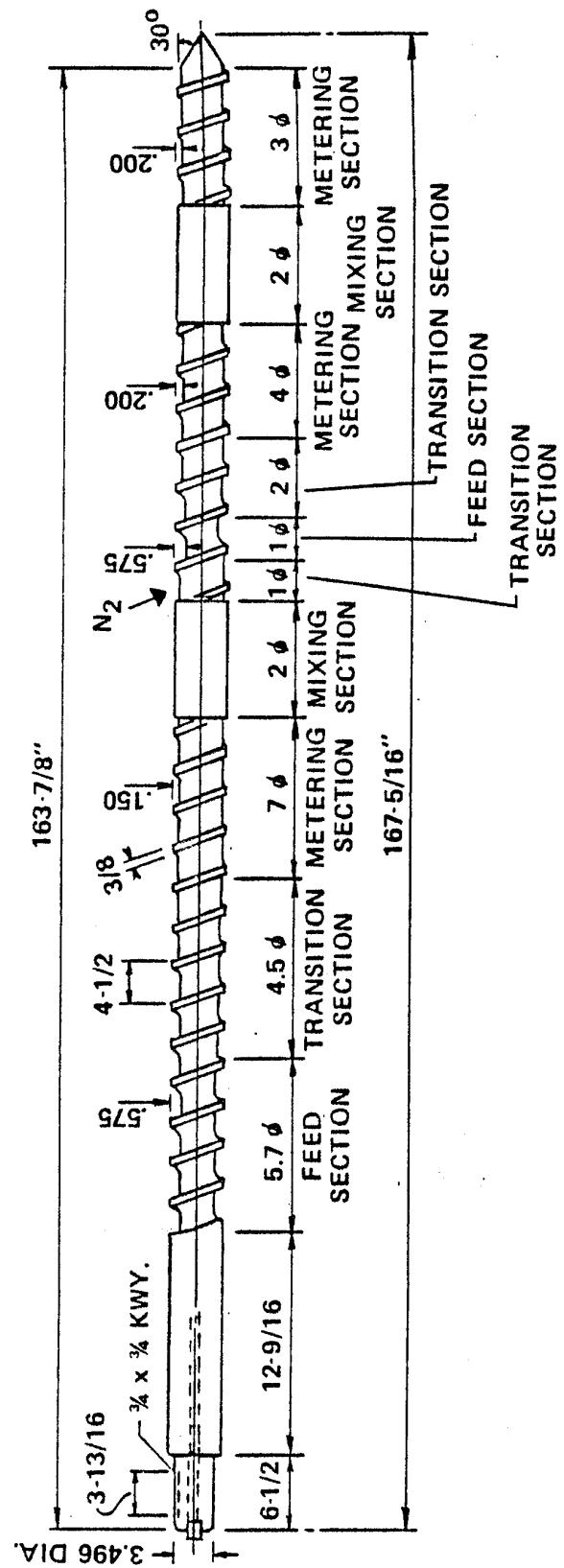
TYPICAL FEED NOZZLE ASSEMBLY

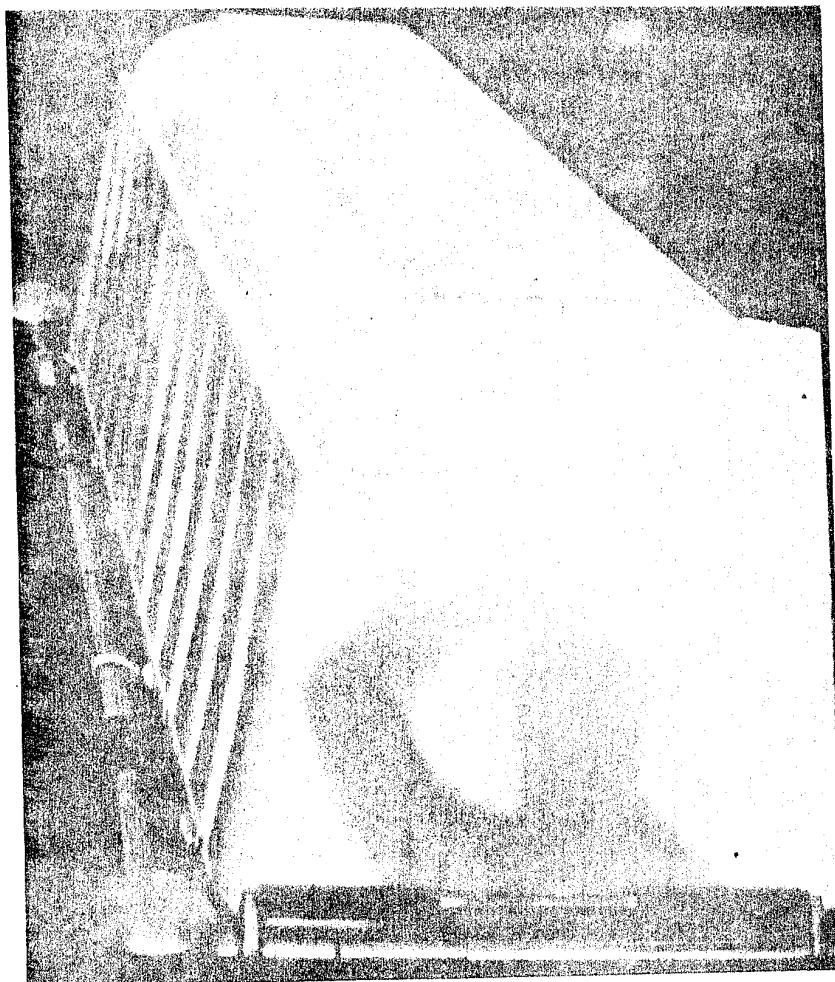


TYPICAL PLATEN LAYOUT 300 TON SF MACHINE



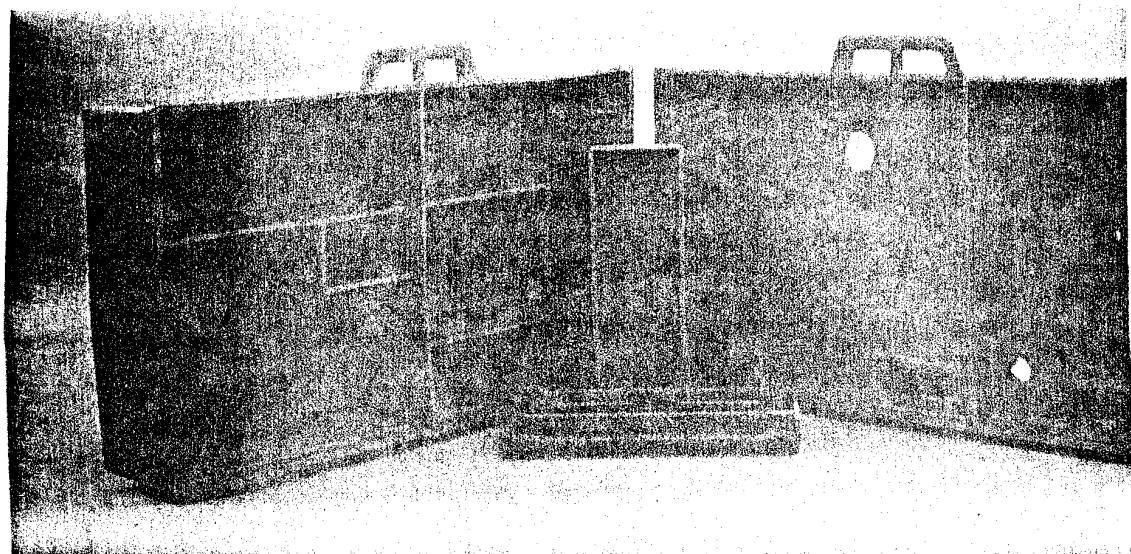
TYPICAL SF EXTRUDER SCREW LOW PRESSURE MACHINE

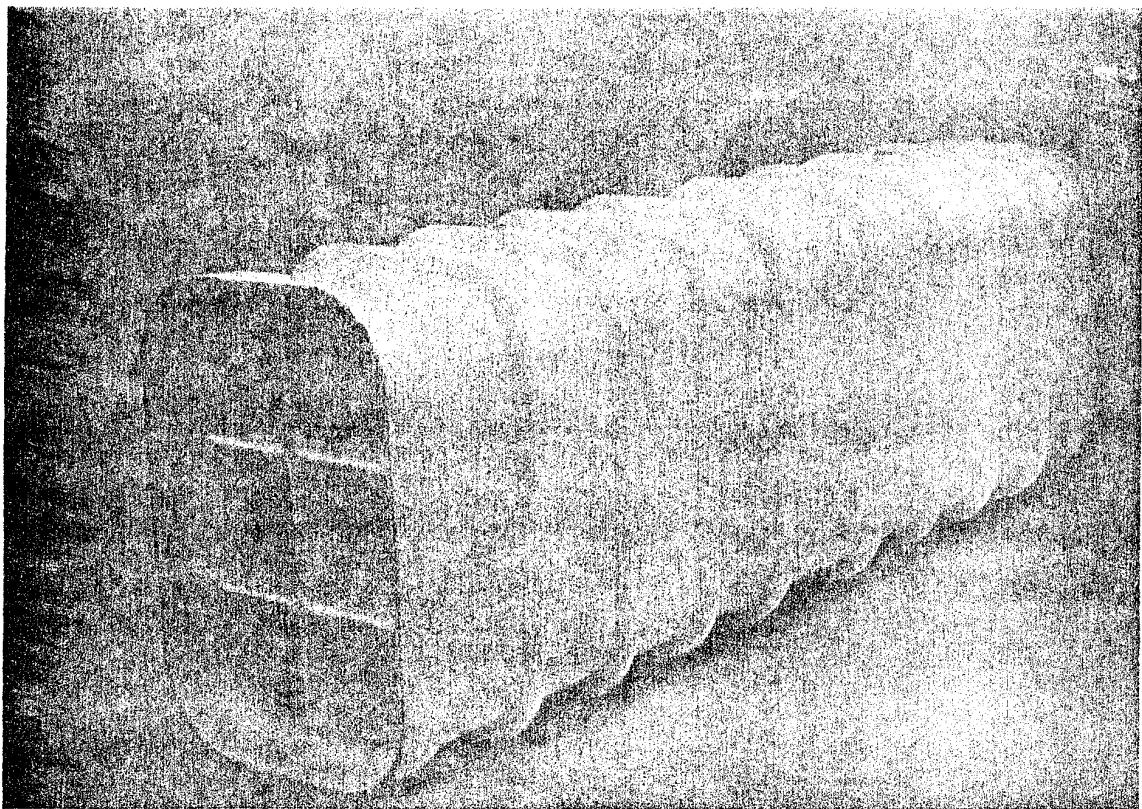




5 - STRUCTURAL FOAM POLYPROPYLENE COFFIN

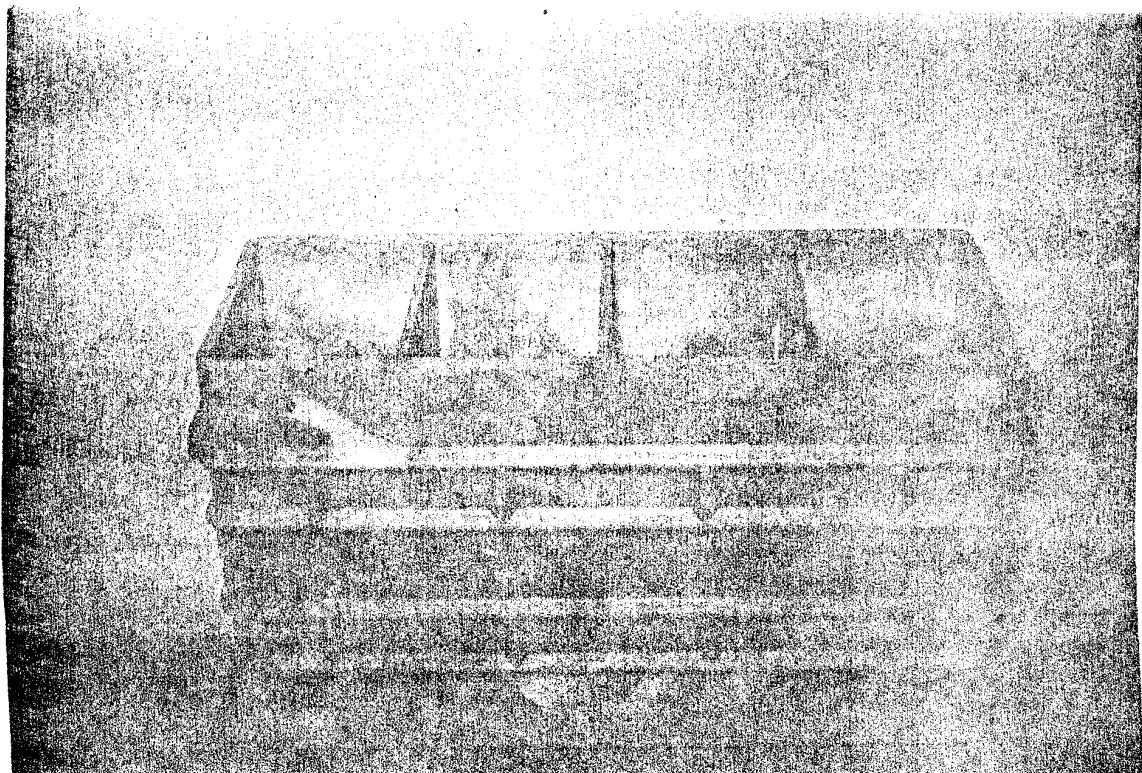
6 - S.F.P.P. TOOL BOX

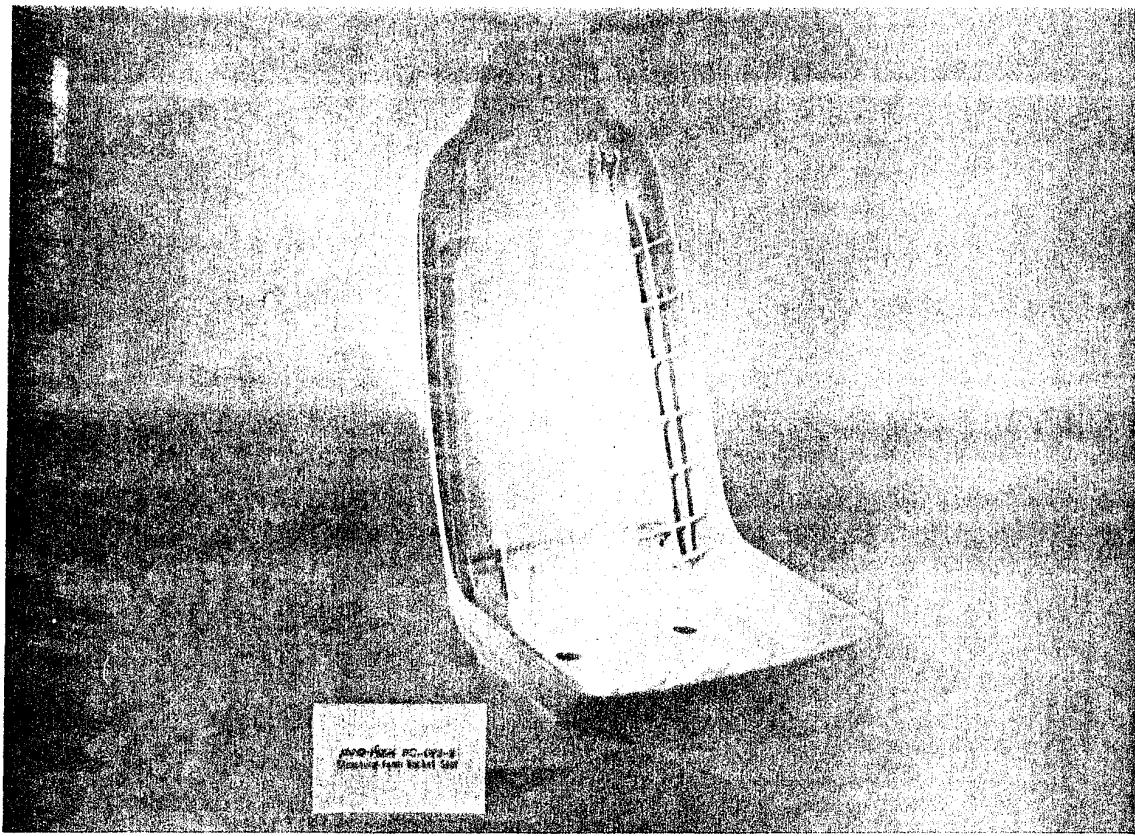




7 - S.F.P.P. DUCTING

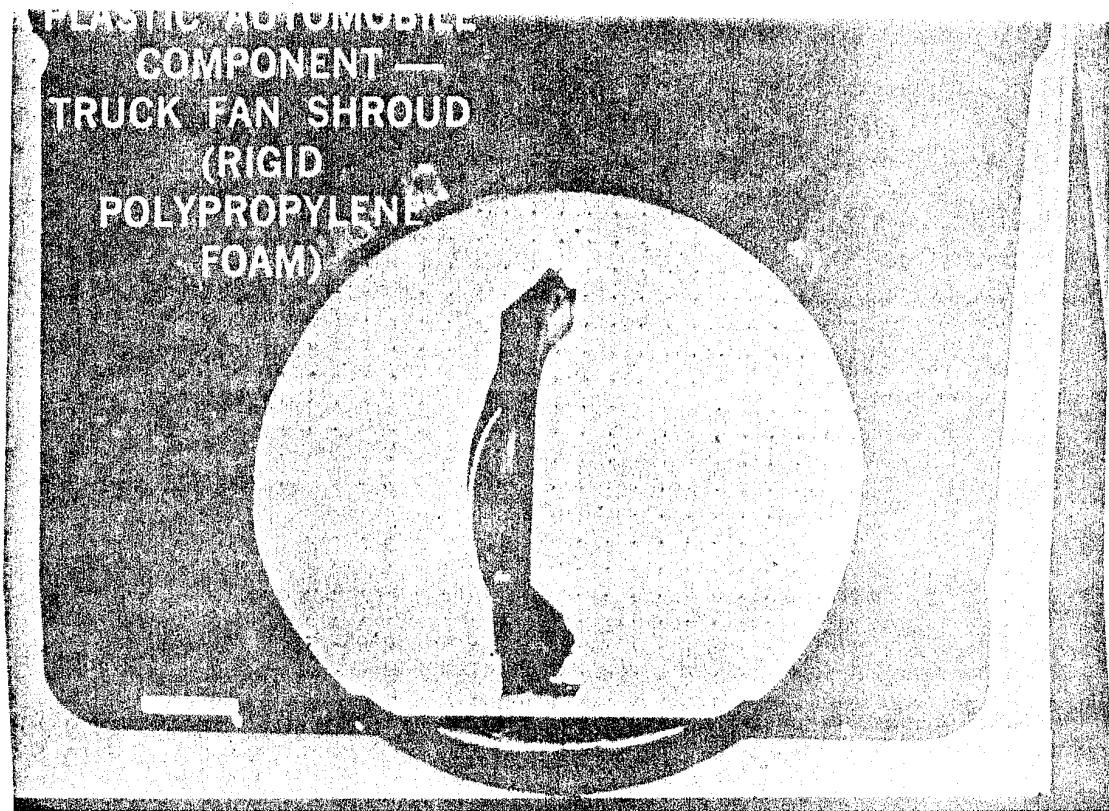
8 - S.F.P.P. HEAVY DUTY BATTERY CASE





9 - S.F.P.P. BUCKET SEAT

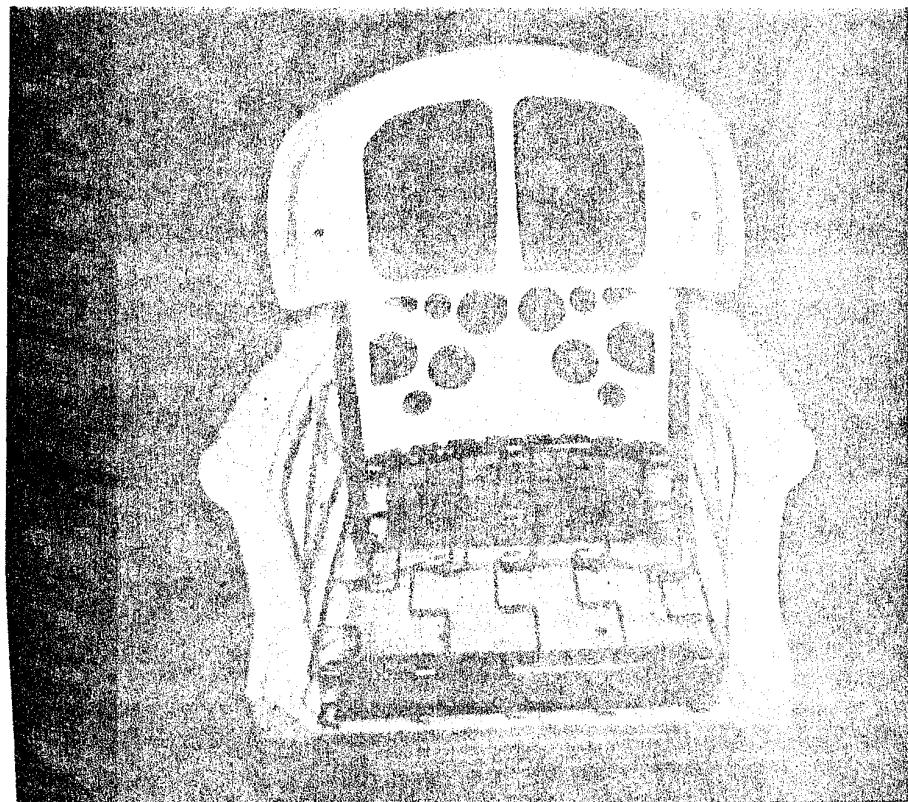
10 - S.F.P.P. TRUCK FAN SHROUD





11 - S.F.P.P. CHAIR FRAME (PARTLY COVERED)

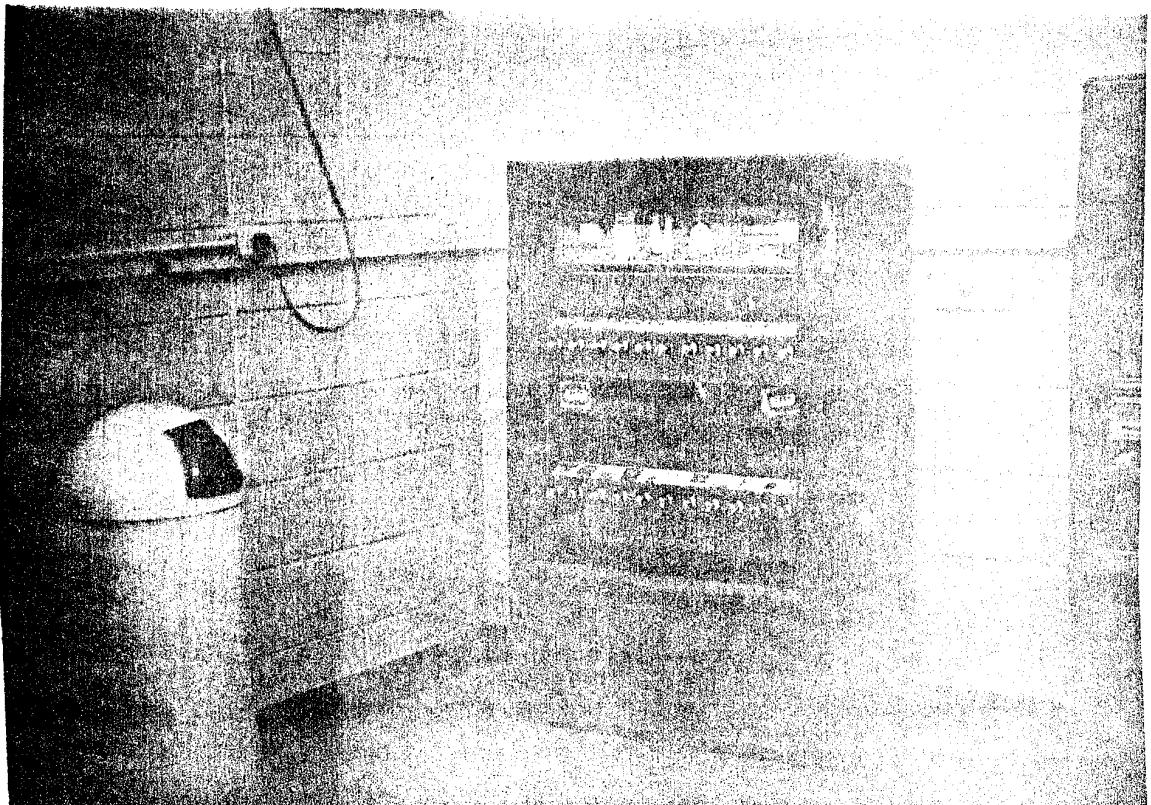
12 - S.F.P.P. CHAIR FRAME





13 - S.F.P.P. STORM DOOR

14 - S.F.P.P. VENDING MACHINE



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*F. Staempfli
A. K. S.
✓*

CONTINUOUS GLASS REINFORCED POLYPROPYLENE LAMINATE
"AZDEL"
processing and applications

Dr Eduard K. STAEMPFELI

General Manager of SYMALIT SERVICE AG

Bahnhofstrasse 30

CH-8022 ZÜRICH

E

Glass mat reinforced thermoplastics - a new material

Processing and typical applications of glass mat reinforced polypropylene

By E. K. Staempfli, Symalit Service AG, Zurich, Switzerland

1. Introduction

The impetus for the development of glass mat reinforced, thermoplastic semi-finished materials was the fact that chopped fibre reinforced thermoplastics had certain disadvantages, as well as experience in the field of polyester sheet moulding compounds (SMC).

The good mechanical strength properties of chopped glass fibre reinforced thermoplastics - which are processed mainly by injection moulding - can only be applied to finished articles up to a point, because orientation of the glass fibres occurs during processing and is difficult to influence. This orientation can lead to considerable variations in strength of the finished article. The strength at right angles to the fibre direction is often not even as high as that of the basic, unreinforced material.

Mouldings made from glass mat reinforced thermoplastics, on the other hand, are very uniformly reinforced and thus largely combine the advantages of unsaturated polyester resins, e.g. high strength and rigidity which is maintained in all directions, coupled with the processing advantages and design latitude of thermoplastics.

Glass mat reinforced thermoplastics are processed, like polyester SMC's, by flow moulding, using high speed moulding presses. The cut-to-size blanks are heated and moulded in the cooled mould, using very short cycles, whereas cold polyester SMC blanks are moulded in a heated mould with very much longer moulding cycles.

2. Production of semi-finished material.

Glass mat reinforced polypropylene laminates are manufactured continuously, several layers of glass mat, impregnated with a special polypropylene melt, being combined to form an endless, completely impregnated sheet material.

The standard content is 40 % w/w.

In contrast to all other glass fibre reinforced plastics, glass mat reinforced polypropylene laminates are made with endless glass fibre mats, achieving a particularly good reinforcing effect. The special structure of mats made from E-glass facilitates good flow of mat and melt, so that the glass fibres become evenly distributed right to the edge of the finished moulding.

The sheets and cut-to-size blanks can be stored indefinitely and are at the moment available in black and natural colour. Other materials such as decorative laminates, films and textile covering can be laminated on top of these sheets during manufacture and, in some cases, during the actual moulding or forming process.

3. Fabrication of semi-finished materials.

The semi-finished glass mat reinforced polypropylene laminate material is normally cut into rectangular pieces already in the production line and supplied in blanks or sets of blanks whose volume corresponds to that of the article to be made. Fabricators are therefore not involved in costs for cutting to size, scrap disposal and weighing out.

The size of the cut blanks and their arrangement in the mould, are first ascertained by preliminary tests. These factors largely determine the economic production and the quality of the finished mouldings.

Cut-to-size blanks are always smaller than the moulding surface. In practice, several blanks, arranged on top of each other, are often used.

The blanks are best heated to the forming temperature of around 200°C by means of infra-red heaters. Because of the poor thermal conductivity, it takes longer to heat up the material than to form it so that several pieces must be heated simultaneously. Infra-red ovens should therefore be equipped with an intermittent advancing mechanism cycling device and have individually controllable zones to enable the material to be heated without the risk of thermal degradation.

Prototype moulds are usually cast from zinc alloy. Prototypes can often also be made with tools used to process polyester resins or for making injection mouldings.

For large-scale production one uses cooled steel moulds (e.g. C 60) with a strength of at least 80 kgf/mm^2 . The mould surfaces are polished and, in certain cases, hard chromium plated. The mould cavity is sealed by hardened, vertical flash faces (max. clearance 0.02 mm for flash-free mouldings; min. height 12 mm). Vertical flash faces must never be used as a means of guiding the mould.

The mould does not close on to distance pieces but on to the moulded glass mat reinforced polypropylene component. This compensates for shrinkage of section thickness (up to 10%) and blank tolerances.

The high lateral forces often encountered during moulding must be absorbed by a robustly constructed and accurate mould guiding system.

Moulds are usually equipped with ejector pins and vents.

The shrinkage in length and width of 1 - 3% is not normally taken into account when designing the mould.

Short cycle times of 20 - 50 seconds require the mould to be cooled to 25 - 60°C.

In practice, the heated blanks are usually put into the mould by hand.

No special equipment or controls are required for moulding presses.

Pressures between 100 and 170 kgf/cm^2 are necessary to achieve a good quality article with a smooth surface finish, depending on the shape and section thickness of the moulding. The higher figures apply to section thicknesses less than 2 mm and to mouldings with surfaces which form a small angle with the direction of press stroke.

Fast cycling presses, which attain the required moulding pressure within 6 - 10 seconds of the blanks being put in position, prevent excessive cooling down of the heated blanks before they are moulded into shape.

Articles with varying cross-section can be produced, e.g. with glass mat reinforced ribs, attachments and studs.

Hydraulic presses are normally used, but it is also possible to use very rigid mechanical presses which should be equipped with coupling and brake. The stroke is arrested at the lower dead-centre and the unlocked, stressed press can relax as the moulding shrinks.

Cycle times with cooled moulds are between 20 and 50 seconds, i.e. about 4 - 5 seconds per mm section thickness. Taking into account the time necessary to put the blanks in position and to demould the finished article, 60 - 150 mouldings can be produced per hour in continuous operation, with a reject rate of 1 - 3 %. Any scrap or rejects that are produced can be reground and - unlike SMC scrap - be re-processed by extrusion or injection moulding.

In practice, all additional operations such as punching of holes and slits, moulding-in of inserts, deflashing etc. are carried out simultaneously after flow moulding in suitable equipment.

Mouldings can be of any size required. Section thicknesses of between 1 and 7 mm are normal and reinforcements up to 15 mm thick are often encountered.

Sharp edges are possible, although not recommended from the moulding point of view. The minimum taper, depending on the depth, is 0 - 3° and more for textured surfaces. Recesses and holes parallel to the moulding stroke can also be produced during the moulding operation. Holes in other directions and deep undercuts can only be produced in specially designed tools. Inserts can also be incorporated.

4. Cost-benefit comparison

Table 1 contains information about the cost-benefit question. The cost of materials for glass mat reinforced polypropylene articles is already less on a volume basis than that of several of the listed reinforced thermoplastics, aluminium and steel, because of the lower density.

More important, however, is the fact that short production cycles, coupled with relatively low capital outlay for presses, equipment and tools, result in lower manufacturing costs compared with competitive processing techniques.

If one compares the mechanical data given in table 1 one must take into account the fact that the figures for chopped glass reinforced thermoplastics were generally determined on test bars in which the glass fibre direction and the direction of loading largely coincide. At right angles to the fibre direction the figures are, however, much lower. In the case of glass mat reinforced polypropylene mouldings where the reinforcement has a random distribution, on the other hand, there are no marked differences between the mechanical strength in longitudinal and transverse direction.

The service temperature is extended both at the cold and the hot end of the temperature scale compared with similar chopped glass fibre reinforced polypropylene injection moulding grades. Falling dart test at -40°C give very good results for GPL, comparable with those obtained with SCM.

GPL components are, above all, in competition with deep drawn sheet metal parts, injection mouldings made from engineering thermoplastics and mouldings made from glass fibre reinforced UP resins.

Mouldings made from glass fibre reinforced polyester resins are, above all, more rigid and heat resistant than mouldings made from glass mat reinforced polypropylene.

The final texture of mouldings produced from UP prepgs is attained only in the heated tool. This is one of the reasons for the still relatively wide variations in quality from one batch to the next. In flow moulding of GPL, the thermoplastic material is only shaped or formed in the tool and this permits narrower quality limits to be observed.

Development work still needs to be done for both materials as regards the mass production of components with perfect surface finish. Surface finish and appearance (colour and degree of gloss) of components made by either method are still not up to the standard achieved with painted metal parts. In the case of mouldings made from SMC there are difficulties especially as regards surface blemishes such as voids, pores (both of which can cause blistering during painting) and stray glass fibres on the surface, faults which can be detected only with great difficulty when the mouldings are visually inspected. The consequence is large numbers of rejects and high finishing costs. GPL mouldings are solvent-free and therefore do not tend to form blisters or holes when being enamelled. As far as stray glass fibres on the surface are concerned however, they behave similarly. This disadvantage can be eliminated by texturing the surface.

The insufficient temperature resistance of GPL makes it impracticable to dry painted GPL parts in paint drying ovens commonly used today in the car industry.

For many mechanically stressed mouldings it is much more important to use a material with great toughness and adequate strength. The greater toughness of GPL increases the energy absorption without permanent deformation, as can be seen in table 2 from the shaded areas, compared with glass fibre reinforced SMC. Because of this great toughness, couples with adequate rigidity, GPL is particularly suitable for seat shells, bumpers, shells for suitcases and similar moulded components. SMC mouldings have a greater tendency to form hairline cracks under conditions of stress and sudden loading, because of their greater rigidity, as well as sharp-edged breakage at critical points.

Compared with mouldings made from SMC, GPL mouldings can be made much more quickly and with much lighter weight. The cost advantage of SMC is largely compensated by the much higher density already if one makes a volume comparison. If one furthermore considers the two to three times longer production cycles for SMC based mouldings, the resultant higher costs for a certain capacity, and the greater quantities of scrap, which cannot be reused, considerable cost advantages often result for the same components made from GPL.

The main advantages over deep drawn sheet metal components are lower weight, better corrosion resistance and the inexpensive integration of several product functions in one moulding. The last point also applies to more complex deep drawn metal parts which are made in several deep drawing tools, often with annealing in between. Tooling and production costs per item are, in such cases, often less for glass mat reinforced polypropylene laminates than for metal parts.

If maximum mechanical strength, smooth surface finish and ease of painting are of prime importance, sheet metal has a definite advantage.

Compared with injection mouldings made from reinforced or non-reinforced engineering thermoplastics, the notable features include the mechanical strength which is more or less the same in all directions, improved service temperatures and the higher impact strength. The somewhat shorter production cycles for GPL mouldings are important for the cost per item but especially as regards investment for machines and tools.

Medium and large size flat components with slight as well as considerable differences in section thickness can often be made very much more easily, and with fewer stresses, by the new flow moulding technique. Moreover, injection moulding of such parts becomes technically difficult and economically infeasible with increasing size.

5. Typical applications

The following examples of typical end uses are parts which have been mass produced in the USA for a number of years.

Fig. 1 shows a lawnmower shroud base weighing 370 g; wall thickness 2.5 - 6.2 mm, dimensions 380 x 355 x 145 mm, output about 200'000 p.a. A cooled steel mould is used and it takes 30 seconds to produce this component, the reject rate being 1-3 %. The component replaces six punched metal parts, one cast aluminium part, seven nylon inserts and several screws and spring washers, the component and tooling costs being slightly less and resulting in a component which weighs less and has better corrosion resistance. The housing reduces noise and is vibration-damping, is placed around the cylinder head and must carry out load-bearing functions at service temperatures of around 110°C.

Fig. 2 shows a battery support for a car (weight 405 g; wall thicknesses 3.8 - 6.4 mm with 16 mm thick ribs, dimensions 203 x 254 x 100 mm with undercuts, output 600'000 p.a.; cooled steel moulds with two cavities). The part replaces a deep drawn sheet metal component because of its lower cost and weight, corrosion resistance and greater design latitude.

The mass produced article shown in fig. 3 is the front end retainer for the flexible PU front part of a car (weight 3600 g, wall thickness 3 - 13 mm, length 1720 mm, output about 200'000 p.a., cooled steel mould, moulding cycle 50 seconds, reject rate 1-2 %). The saving in weight compared with a similar, multi-component deep drawn sheet metal part is around 60 - 70 %. The advantages are: no interference with headlight adjustment at component temperatures of 90°C; adequate rigidity; adequate toughness to absorb torsional loads during assembly and if there is a head-on crash; saving in material and tooling costs; corrosion resistance.

The guitar case shown in fig. 4 (weight without fittings 3000 g, wall thicknesses 2.5 - 3.8 mm, dimensions 1040 x 380 x 127 mm, output about 35'000 p.a.; one cooled steel mould per half case, moulding cycle 40 - 45 seconds, with post-cooling arrangement). This article has successfully passed tests which involved comparison with vinyl covered wood and cardboard cases, thermoformed and injection moulded ABS cases and SMC cases. Advantages: untreated, textured surfaces meet aesthetic demands; adequate protection of the guitar, even if sent by road or rail transport; cost saving compared with alternative solution; simple design which dispenses with an aluminium frame.

A particularly interesting example is shown in fig. 5, which consists of a two-part seat shell for a car (Base: weight 2100 g, wall thicknesses 3.0 - 6.3 mm, dimensions 530 x 480 x 75 mm. Back: weight 1400 g, wall thicknesses 3.0 - 6.3 mm, dimensions 500 x 350 x 60 mm, output about 45'000 . One cooled steel mould per part, moulding cycle 40 - 50 seconds). The advantages in this case include a saving in weight compared with a conventional, steel seat (4,700 g per seat), textured and painted surface where the component is visible and great toughness as the most important safety consideration.

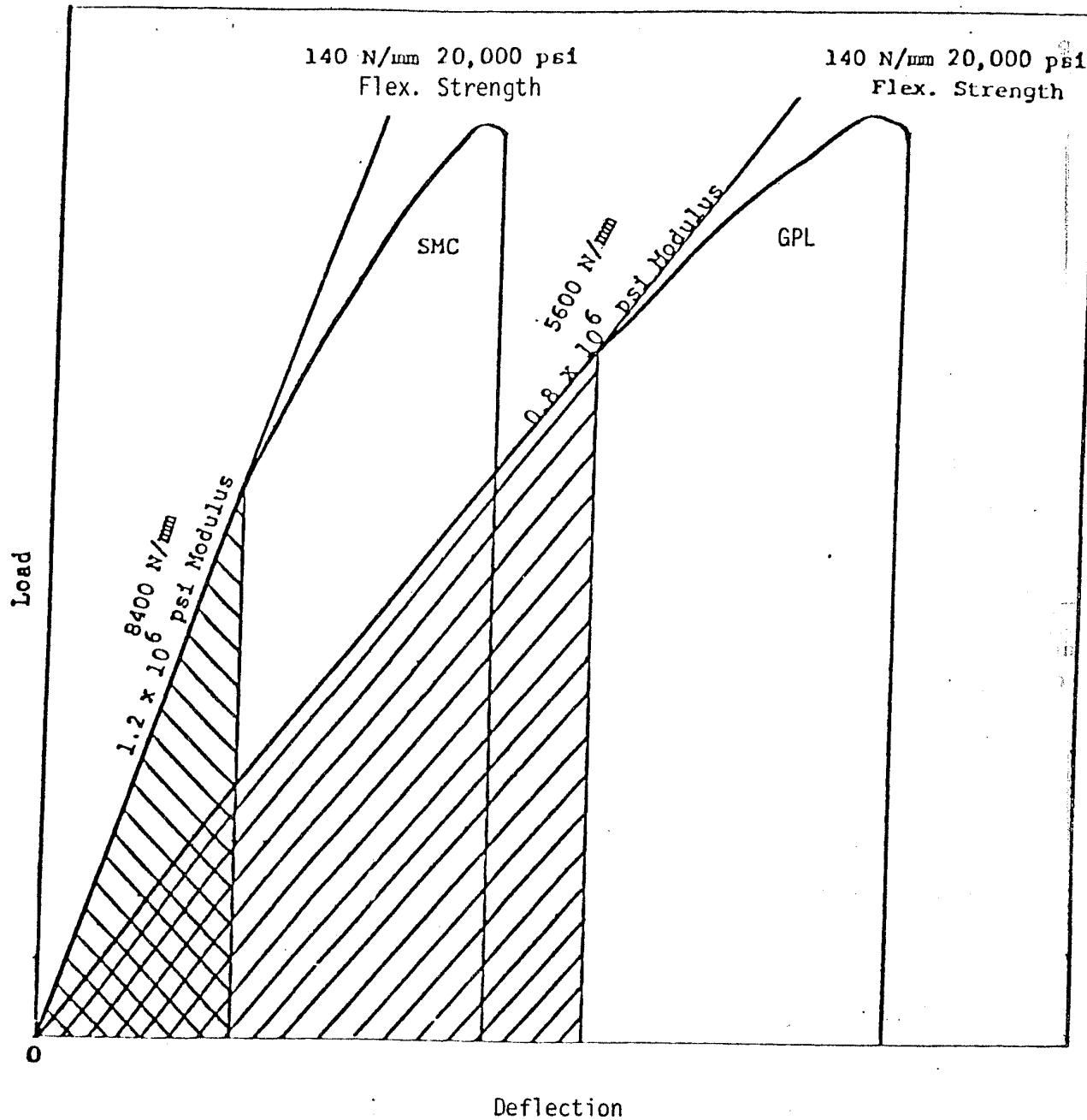
Table 1. Price and property comparison

	Price index* related to		Density (g/cm ³)	Flexural strength (N/mm ²)	Flexural modulus of elas- ticity (N/mm ³)	Notched impact strength (J/m)	Heat resistance (°C)
	same weight	same volume					
GPL (40 %)	100	100	1.19	155	3600	535	155
Polypropylene/ glass fibre (40%)	71	74	1.22	77	3600	144	135
Nylon/glass mat	115	135	1.37	162	3600	43	200
Nylon/ glass fibre	112	130	1.36	176	8400	160	210
Polycarbonate/ glass fibre	144	164	1.35	134*	3600	107	142
Polycarbonate structural foam	128	91	0.80	70	2100	-	132
ABS, unirid foriced	56	50	1.04	67	2300	128 to 390	90
SMC	57	91	1.60 to 1.90	125 to 200	7000 to 11200	615	190 to 260
Fibrel	-	-	0.70	37	-	-	125
Aluminum	63	135	2.76	-	0.76 · 10 ⁴	-	-
Steel	19	130	7.83	-	2.10 · 10 ⁴	-	-

(-) values not available

*based on US prices, GPL = 100

Comparison of Flexural Properties GPL vs. SMC



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ULTRAHIGH MOLECULAR WEIGHT POLYETHYLENE
PROPERTIES and APPLICATIONS

Herbert MROZIK

Technik & Marketing G U R
Ruhrchemie AG

D-4200 Oberhausen-Holten

Properties and applications
of THE ULTRA HIGH MOLECULAR WEIGHT POLYETHYLEN

(HOSTALEN GUR)

With increasing molecular weight technically important properties of HDPE are improved. They reach an optimum in U. H. M. W. PE around 3.5 million.

A special characteristic of Hostalen GUR is

- high impact strength
- outstanding wear resistance
- low coefficient of friction
- resistance to chemicals

the U. H. M. W. PE has a wide variety of application areas, not based on one property, but usually on several of its attributes.

One unique application is in surgical implants, where the material has been used in artificial hips and other devices that require wear and impact resistance plus compatibility with the human body.

Examples of other applications are wear resistant sheets in chutes and liners of bulk-material-handling systems and many parts in beverage, textile, chemical and paper industry.

Last but not least applications have been found in sporting equipment, such as ski bottoms, toboggan and ice-skating surfaces.

Properties and applications of the U. H. M. W. PE

OP

Synthesis of polyethylenes

The polymerisation of polyethylenes is carried out either under high (2 000 bar) or low pressure.

The high pressure synthesis produces filamentary molecules with side branching. The distance between the long sides of the molecules is thus increased, making the product more plastic.

Ziegler's low-pressure method produces a linear polyethylene. According to the choice of a suitable catalyst, products of high or low molecular weight can be achieved.

1. Properties of the U. H. M. W. PE

With increasing molecular weight, a number of technically important properties are improved, reaching an optimum around 3.5 mill.,

Such properties are, above all:

Slide 1 a) resistance to wear
 b) impact resistance
 c) low coefficient of friction
 d) resistance to chemicals
 e) stability of form on change of temperature

The density also has a considerable influence on the properties of a polyethylene.

Tensile strength, rigidity and hardness depend directly on the density.

1.1 Impact resistance

A special characteristic of the UHMW PE is the high impact resistance, which reaches good values even at extremely low temperatures.

Slide 2 shows the impact resistance of the UHMW PE at low temperatures. The impact resistance is shown on the ordinate axis, temperatures between -200°C and +120°C on the abscissa. Even at low temperatures, possesses a toughness surpassing that of all other plastics to date.

At the temperature of liquid helium, -269°C, the UHMW PE withstands a certain shock stress without splitting. Thus parts such as seals and packings have proved themselves in reciprocating pumps for liquid helium (-269°C). Pistons of high quality chrome-nickel alloy steel

showed such a high rate of wear at these temperatures that the efficiency was reduced after a short time. They were then coated with a layer of UHMW PE. Even after being in use for a full year, there was no noticeable drop in efficiency. On dismantling for control purposes no visible wear could be detected; the pistons could be re-fitted. This shows that excellent sliding properties are retained at extremely low temperatures.

1.2 Frictional properties

Slide 3 gives a survey of the coefficients of sliding friction of various plastics on a polished steel surface. Plastics such as UHMWPE, Nylon, PTFE and acetal resins are compared. Dry friction, as well as lubrication with water and oil gave rise to frictional values very nearly comparable with PTFE.

1.3 Resistance to wear

Resistance to wear is a property of the UHMW PE which is particularly striking. In several special cases it is superior even to high quality steel alloys. The Sand-Slurry Method, a means of measuring wear which tests the materials especially hard, gives a clear indication of the possible applications of Hostalen GUR. The test pieces rotate at 1.200 rpm for 24 hours under defined conditions in a sand-water slurry.

In slide 4 specimen of various materials are shown

- I. Hostalen GUR original test sample.
- II. Hostalen GUR after the test. Hardly any signs of wear can be recognised.
- III. Steel ST 37. Rounding off of the opposite corners can be clearly seen. The volumetric wear is 60 % more than with Hostalen GUR.
- IV. PTFE. Signs of wear along the whole length. 430 % more wear.
- V. Polymethylmethacrylate. 1 700 % more wear.
- VI. Beechwood. 2 600 % more wear.

1.4 Stability of form on change of temperature

Due to the high molecular weight, Hostalen GUR can be used without problems at steady temperatures up to 80°C. Even at temperatures far higher than the crystalline melting range (135°C), due to the high viscous elasticity, the product still shows a certain stability of form. Under special conditions, however, applications are possible at much higher temperatures. In the production of sulphuric acid, for example, jets made of Hostalen GUR (see sample a) are used at 450°C in the sulphur dioxide washers and last for 2-3 years, as a result of the rapid charring of the surface. In another chemical plant, the sealing flanges between the metal reaction vessel and the glass pipes were made of Hostalen GUR, although a mixture of hydrobromic and glacial acetic acids are allowed to react at 130°C in the vessel. After being in use for 52 months the flanges still sealed. Here, too, after dismantling, a thin layer of carbon could be seen on the reactions side of the flange (sample b), which serves as a protection against further attack.

1.5 Resistance to chemicals

The examples given demonstrate very clearly that Hostalen GUR has an exceptional resistance to chemicals. Only strongly oxidising acids attack the material. Aromatic and halogenized hydrocarbons, which dissolve PE-types of low molecular weight, merely cause swelling of Hostalen GUR. The reason is that the resistance of polyethylene to stress corrosion increases with the molecular weight.

2. Processing of the semi-finished product

In the production of finished parts from Hostalen GUR, a primary concern is processing to remove internal stresses. If the finished products have to comply with higher standards of dimensional conformity, especially when subject to changes of temperature, tempering of the semi-finished product between 100°C and 160°C, according to the demands, is advisable. This tempering removes internal stresses caused during manufacture to a very large extent. Hostalen GUR can easily be sawn, turned, planed, milled, drilled, punched and welded, suitable machines being those typically used for metal- and woodwork.

2.1 Processing of UHMWPE

Because of its very high melt viscosity plastification of UHMWPE is carried out mainly by compression moulding. The mould required is of the punch and die type with the required cavity depth.

For the preparation of highest quality sheet and supplementary heating and cooling of the mould chase is advisable. The powder is charged into the mould, levelled off with a straightedge and cold compressed for 5 - 10 minutes under a specific pressure of approximately 100 bar. By this means most of the entrapped air in the powder is expelled.

To melt the charged powder, the press is heated to about 200 - 220°C. Heating at this temperature is continued until the powder is plastified. At this stage the pressure should be in the range of 20 - 50 bar. Heating time depends on thickness of the block. 30 mm require approx. 3 h. The mould chase is heated only in the last stages of this period.

After that cooling is applied. A slow pressure rise is required up to 100 bar. During the first part of the cooling cycle, cooling on the chase must remain off in order to obtain block free from sink marks, since through side cooling the material solidifying first at the edges adsorbs the pressure which then has no effect on the centre of the block, where the material is still plastified.

Due to its high molecular weight and associated high melt viscosity UHMWPE cannot be extruded by ordinary methods. Special additives however make twin screw extrusion with co-rotating screws possible. Extrusion is carried out at screw speed of about 10 rpm and temperature in the region of 180-200°C. Special attention should be given to the die design. The flow paths must be constructed adequate in length so that the individual melt strands from the breaker plate, fitted beyond the screw, are satisfactorily fused together.

To keep the extrudate free of voids long cooling zones are important. Large cross section profiles for example require cooling zones of 20 m or more.

In addition to twin screw extrusion, ram-extruder as used in KTE may also be used with excellent results.

The operation is as follows:

The powder is charged in portions via a hopper into the barrel of the ram-extruder, where it is compressed by a plunger, the so called ram. The material passes the heating zones of the die where it gets plastified. The die must be long enough to plastify the powder completely. The weld lines which occur with each ram stroke fuse completely, so that a homogeneous solid profile is formed. The processing temperature range is 200-220°C. The cooling is comparable to twin screw extrusion.

3. Possible applications

3.1 Lining of containers as protection against bridging, abrasion and corrosion

In numerous industrial plants, raw materials, intermediate products and finished products are often stored in large concrete or steel bunkers in order to be able to maintain production continuously. As a result of the poor flowing properties of the bulk materials, problems are often caused by bridging in the bunkers and sticking in the chutes.

As solution to these problems, shown by years of experience to be effective, has been found by lining the bunkers with sheets of UHMW PE.

Due to their surface being similar to paraffin wax and thus having low-friction properties, the UHMW PE sheets avoid sticking and, at the same time, possess extraordinary abrasion resistance. The fact that the material absorbs no water and the high resistance to tension cracking and corrosion also allow applications where bulk materials are moist and aggressive.

3.1.1 Concrete bunkers

Concrete bunkers in which fine coal with a moisture content of 10 % and more was stored and with which there were problems, above all in winter, were lined with 6 mm thick sheets of UHMW PE.

Slide 5 shows details of the lining.

The sheets were fitted vertically without any gap and horizontally overlapping in the direction flow by 30 mm.

3.1.2 Steel bunkers

In various chemical plants in which moist materials or those with a strong tendency to stick or corrode (e.g. iron pyrites, purple ore, common salt, etc.) are stored in steel bunkers, the inner walls of the bunkers have for years been lined with sheets of UHMW PE. The sheets are fitted as in concrete bunkers.

Slide 6

Steel bunker in a coal-fired power station.

Due to the extremely unfortunate geometry of the bunker itself, bridging was always causing problems. Lining the bunker was the solution. Since then, the plant has been trouble-free.

Linings can be used with almost any bulk materials, such as lime or cement, which tend strongly to bridging due to being so fine-grained. Even these can be made to flow by using Hostalen GUR.

The following angles of slip were measured when using limestone of various particle size distribution:

Hostalen GUR	11 - 18°
concrete	35°
steel	30°

With dry, powdery materials which tend to build up static electricity it is advisable to use Hostalen GUR anti-static for the lining. This material has a surface resistance greater than 10^6 ohm.cm and ensures protection from electrostatic charging.

3.2 Pipes made of Hostalen GUR

The transport of solid materials through pipes is becoming more and more rationalised. The hydraulic transport of solid materials is becoming especially important.

This method can be troublesome when abrasive materials are to be transported. The decisive factors are wear and energy requirements. Pilot experiments have shown that for various types of sand, for example, the loss of pressure in plastic pipes is about 25 % lower than in steel pipes. This means a considerable saving in energy. Further, the lower friction in Hostalen GUR piping means that the critical velocity can be reduced by up to 12 %.

Present experience shows that Hostalen GUR is also better than steel with respect to wear resistance. A comparative analysis showed abrasive wear of 17 g/m for Hostalen GUR, but 400 g/m for steel piping ST 35.8 under equal conditions.

3.3 Implants

Medical progress has led to sensational developments in joint surgery. Whereas such operations used to be much feared, the last few years have seen a steady increase in the replacement of joints which have been damaged by arthritis or accidents. The artificial hip joint has been especially prominent in this field of development.

Slide 7 Hip joint

The suitability of a material for implants is determined by the combination of a number of important properties. In this respect frictional and wear properties of the moving parts must be emphasized. Due to its structure - similar to that of the paraffins - UHMW PE possesses excellent sliding properties. Further, due to its extremely high molecular weight, it possesses an optimum toughness.

Slide 8 X-Ray photograph of an implanted hip joint

A surgical material which is to be implanted into the body must fulfill still further conditions. Thus, it is essential that it does not contain any toxic substances and that it does not cause any pathological reaction in the tissue. By means of extensive biological tests on the one hand and 15 years of clinical experience on the other, it has been confirmed that the UHMW PE fulfills all these concitions ideally.

3.4 Conveying techniques

Slide 9 The filling of bottles

High resistance to abrasion and especially its sound-damping properties make Hostalen GUR indispensable. Dog-bone profiles allow high conveying speeds and protect from glass breakages at the same time. Driving chains also glide trouble- and maintenance-free on glide rails of UHMW PE. Further parts which are used here are radial and screw conveyers.

3.5 Textile industry

The textile industry makes particular demands on the impact resistance of many machine parts. Whereas for the production of pickers, lug-straps, lug-caps, etc., raw buffalo skin or fabric-reinforced rubber was used, now these are made almost exclusively of the UHMW PE.

Slide 10

A few of the parts used in looms are pictured here. It has been shown that loom pickers, for example, made of UHMW PE have a 4 - 5 times higher number of vibrations compared to other materials due to the high impact resistance and work capacity.

3.6 Battery separators

One of the biggest fields of application is in the development of maintenance-free automobile batteries. A special form of UHMW PE has made this possible. It contains a large part of powdered quartz together with an oil filler. This compound is extruded in form of a very thin film, and the oil extracted later on. By this means, the film gets the microporous structure required for use in separators. Due to the high chemical resistance of the UHMW PE the durability of such a battery can be guaranteed.

3.7 Galvanising techniques

Here, too, there are comparable problems. In galvanising plants many parts are to be found which come into contact with corrosive materials such as acids, salt solutions etc. Galvanising drums are especially troublesome in this respect.

Slide 11

Galvanising and phosphating drums of the UHMW PE.

3.8 Skiing

For a long time there has been a trend towards more perfect and ever faster skis. The present world ski production has already reached 18 mill pairs and is a market with a higher than average growth rate.

Ski surfaces of Hostalen GUR can no longer be ignored. The UHMW PE is used especially for the highly stressed racing skis, due to its specific properties. Its capability of taking up a lot of wax, together with the low coefficient of friction make it possible to save the few tenths of a second so important in racing sport.

Slide 12

Toboggan track made of UHMW PE.

Interest in bob- and sleigh-riding increases more and more, but the availability of artificial tracks is particularly poor.

A bob-track made of UHMW PE is being developed. The track is independent of ice and snow and can be used by experts as well as beginners. This is made possible by a choice of suitable materials for the runner surface. Speeds between 12mph and 60 mph approx. are possible.

3.9 Paper industry

the UHMW PE is used in paper-making machines especially because of its excellent wear resistance.

Slide 13

The bronze or plastic sieve carrying the paper pulp runs over the various surfaces while the water is being removed. Despite the very high speed of the sieve in parts, the rate of wear is low. The advantages of using the UHMW PE are: good durability of the sieve, low energy requirements, due to the good sliding qualities and easy reconditioning of the parts used.

Finally, there is a short field excerpt showing one of the newest fields of application.

Film:

The UHMW PE has found a footing even in the field of ice-skating. Ice-skating, which used to be possible only in winter or with the help of complicated cooling systems using large quantities of energy, can now be enjoyed on a summer's day. Sheets of UHMW PE are fitted together underneath by means of tongue and groove or special steel profiles to make a surface as large as required. Due to the low coefficient of friction, ice-skating can be enjoyed on such artificial surfaces with hardly any more effort than usual. Ice-hockey players like these surfaces particularly.

The special advantages of this surface are:

- saving in energy costs
- durability (even intensive use has so far caused hardly any wear in the UHMW PE)
- minimum maintenance requirements

Unfortunately, the short time available did not allow all the possible applications of this material to be shown. However, these examples make it clear that there is hardly a field where the UHMW PE could not be used.

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Gent, Belgium

THE DISKPACK POLYMER PROCESSOR
~ A NOVEL POLYMER PROCESSING MACHINE ~

by

Z. Tadmor, P. Hold, L. Valsamis, O. Duran

Presented by O. Duran

Farrel Machinery Group

USM Corporation

Ansonia, Connecticut

U.S.A.

ABSTRACT

A new polymer processing machine called the DISKPACK* Polymer Processor is presented and discussed. This paper is a summary of two papers presented to the Society of Plastics Engineers' ANTEC Conference in New Orleans, May 7-10, 1979. Entitled "A Novel Polymer Processing Machine - Theory & Experimental Results" authored by Z. Tadmor, P. Hold and L. Valsamis and "Applications & Design of the DISKPACK Polymer Processor" by P. Hold, Z. Tadmor and L. Valsamis. The basic machine has been patented by Z. Tadmor and assigned to the Farrel Machinery Group, Emhart Corporation, Ansonia, Connecticut, U.S.A.

Much of the information contained in this paper is based upon elementary processing steps described in greater detail in the ANTEC papers. Please refer to these two papers for theoretical derivations of solids transport, melting, pumping, mixing and stripping (devolatilization, desolventizing, etc.) Copies of these papers are printed in the 1979 ANTEC conference book.

The DISKPACK Polymer Processor has significant advantages over conventional machinery used today for post reactor processing because its design can be tailored to specific processing functions. These advantages can be expressed in terms of energy efficiency, performance, production capacity, physical size and installation space required.

The machine consists of two or more disc shaped elements attached to a shaft which rotate in a barrel. Polymer is fed through an inlet opening in the barrel to an annular chamber formed by the discs, shaft, and barrel, and is discharged through another opening in the barrel. Inlet and discharge are separated by a channel block tightly fitted into the chamber. The moving discs surfaces drag the polymer in either solid or molten form forward toward the channel block with a gradual buildup of pressure for discharge through a die or for feeding another chamber in series. The DISKPACK Processor is suitable for performing all the basic polymer processing functions; namely polymer melt conveying and pumping, solids conveying, melting or plasticating, stripping and devolatilizing, and both extensive and intensive types of mixing. Moreover, the machine has attractive advantages to serve as a polymerization reactor and desolventizer. The principle of operation for these various processing functions in the DISKPACK Processor are discussed together with a description of how these functions can be combined in one machine.

In conclusion, the basic design information is given of a 15 stage, 350 mm commercial, production size, DISKPACK Processor, as used in our laboratory.

* Trademark applied for by the Farrel Company.

INTRODUCTION

In the manufacturing process of polymeric materials and finished products thereof, three categories of processing machinery can be identified: (Fig. 1.)

- reactor related machinery and equipment
- post reactor polymer processors
- transforming and/or shaping machinery

Depending on the polymerization system and reactor design, a polymer in either melt or particulate form will emerge from the reactor. The majority of polymeric materials will pass subsequently through one or more post-reactor polymer processors for the transformation into a commercial product to be marketed in pelletized form. In this operation, the polymer can be exposed to five elementary processing steps which are defined as (1):

- a - Handling of particulate solids (conveying)
- b - Melting (plasticating)
- c - Pressurization (pumping)
- d - Mixing
- e - Stripping (devolatilization, desolvantization, etc.)

The nature of the elementary steps, their relative significance, and the particular combination selected, determines to a large extent the shape, size, complexity and cost of the polymer processing machine. In case the reactor discharge is in the form of a polymer melt, processing equipment can range from the simple gear pump able to perform only one elementary step (c) to a complex screw extruder capable to homogenize and devolatilize, performing, thereby, three elementary steps (c,d,e).

If the reactor discharge is in a particulate form, batch or continuous mixers can perform the steps of handling, melting and mixing (a,b,d), to be followed in tandem by another piece of equipment for the pumping function. Screw extruders can be designed to perform all the five elementary steps; it will function satisfactorily for some of the steps but at a compromise to the others. To overcome this shortcoming, polymer processors in tandem have been utilized over the last 15 years successfully: as an example, the continuous mixer with extruder installation or twin extruder set-up. However, the great popularity screw extruders have enjoyed (in particular single screw extruders)

is due to their ability to satisfactorily perform most of the elementary steps with a simple and rugged structure.

It is not surprising to find, therefore, that since the invention of the single screw extruder by Mathew Gray* (2), this polymer processor dominates the polymer processing industry with limited (though increasing) challenge from the various types of intermeshing twin screw extruders. There were, of course, many other important inventions through the years, but none of these had the versatility and, therefore, the significance and impact of the screw extruder.

In this paper a novel polymer processor, called the DISKPACK+ Processor (3,4,5), is described. It is radically different in geometrical configuration from all existing processors. This processor appears to have the inherent capability to perform all the elementary steps of polymer processing with greater versatility and efficiency than the screw extruder. Moreover, due to the relatively simple geometrical configuration, most elementary steps can be theoretically modeled, thus greatly simplifying its design, scale-up and development.

GEOMETRICAL CONFIGURATION

The geometrical configuration of the DISKPACK Processor is shown in Fig. 2. It consists of two or more disc shaped elements attached to a shaft placed within a closely fitted barrel. Each two neighboring discs together with the inner surface of the barrel and shaft surface form a single, generally annular processing chamber. The barrel, discs, and shaft are temperature controlled.

The chamber formed by the discs in cross-section can be of a rectangular or wedge-shaped configuration. The difference between the barrel and shaft radii is generally much larger than the separation between the discs. An inlet or feeding port, and a discharge port from the processing chamber is formed by openings through the barrel, as in Fig. 2a. The inlet and discharge port are separated by a channel block which is closely fitted into the processing chamber.

* There is circumstantial evidence to earlier application of the screw extruder.

Processing chambers may be connected in series or they may act in parallel.

THE PRINCIPLE OF OPERATION

The most convenient way to describe the principle of operation of the DISKPACK Processor is by comparing and contrasting it to the single screw extruder. The common and outstanding feature of all elementary steps taking place in the screw channel is that they all are induced by drag brought about by a single moving surface - that of the barrel relative to the screw channel (1,6). Solids are conveyed and compressed by the frictional drag of the barrel surface, and are melted by a drag removal melting mechanism; the melt is pressurized, pumped and mixed by drag induced flow, and finally if devolatilization is needed, it is obtained primarily by repeated spreading of thin melt films on the "moving" barrel surface. The other main surface forming the channel (i.e. the root of the screw) has no "useful" operational function, but "merely" serves as a geometrical boundary. The efficiency of the elementary steps is even retarded by it. Therefore, in search for a better processing configuration, while keeping in mind the nature of the elementary steps, one abandons the traditional screw design and investigates the improvements possible with a geometrical configuration consisting of two jointly moving surfaces. The DISKPACK Processor provides a unique but practical solution to such a geometry.

Pumping

Consider a polymer particle in a melt located somewhere in the processing chamber (Fig. 2). It is confined between the two tangentially moving disc surfaces, dragging the polymer from the inlet to the discharge port. Hence, the basic configuration and simplest model is that of two parallel plates moving at velocity $V_0 = 2\pi NR$, where R is the radial location of the particle and N is the frequency of disc rotation, as in Fig. 3. The barrel surface has some retarding effect on the drag induced by the discs, much like the flights in the screw channel, but partially compensated by the forward dragging action of the shaft surface. Like with the simple screw extrusion model, it is assumed that downstream there is a restriction to flow, such as a die, through which the pressurized polymer is shaped. A theoretical comparison between the two models (of a parallel plate geometry with both plates moving as in Fig 3, versus that with a single plate moving) makes it apparent that:

- the doubling of the drag flow increases substantially the pressurization capability, up to eight fold for Newtonian fluids;
- shear rate is independent of plate velocity since both plates move at the same speed.

If the discharge pressure, $P=0$, then a pure drag flow (plug flow) condition would exist, shear rate and consequently viscous heat dissipation both vanish. With only one plate moving, the shear rate increases with the plate velocity and even in the case of pure drag flow, mechanical energy continues to be dissipated into heat.

The practical consequences of these differences between the two cases are that machines based on relative motion between surfaces, such as screw extruders, upper bounds on plate velocity are set by thermal and shear degradation sensitivity of the polymer.

In conclusion, therefore, we can expect in a machine which is based on the motion of both surfaces at equal velocities, to build up large pressures in short distances with less power consumption.

Mixing

Some insight into the mixing characteristics of a geometrical configuration with both plates moving can be obtained by analyzing the velocity profiles. Fig. 4 shows some calculated velocity profiles with the ratio of pressure flow over drag flow (q_p/q_d) as a parameter. The ratio (q_p/q_d) decreases with increasing pressure rise. With a closed discharge $q_p/q_d = -1$, a circulating flow arises between the parallel plates: polymer melt is dragged forward towards the exit by both surfaces and flows backwards in the center zone. With the discharge opened partially creating a $q_p/q_d = -2/3$, the velocity at the center is zero and no back flow takes place. For a given net flow rate and plate velocity V_0 , maximum pressure rise can be obtained in a condition where $q_p/q_d = -1/3$. At a complete opened discharge the expected plug flow velocity profile returns.

With regard to mixing, the DISKPACK geometry offers some unique advantages. In addition to the above mentioned, predictable, vigorous circulatory flow pattern (controllable by disc speed and discharge rate)

which imparts extensive mixing, the following opportunities arise: mixing blocks of various shapes can be inserted externally through the barrel into the processing chamber. These mixing devices can impart both extensive and intensive (dispersive) mixing. Polymer melt may be recycled over the channel block leading to dispersive mixing and back-mixing; the new processor lends itself both to batch and continuous mixing; solid or liquid feeding is possible, connecting the processing chamber in series further increases its mixing capability, as well as enabling optimal order of ingredient feeding. Preliminary experimental results verify these expectations. Indeed, it appears that the DISKPACK Processor offers the first truly flexible polymer processor-mixer configuration.

Solids Handling And Melting

Turning to the other elementary steps, similar advantages are evident. In solids conveying, just like in pressurization, there are two forward dragging surfaces greatly enhancing the conveying capacity. In melting, forced drag induced melt removal can be achieved on both surfaces as indicated schematically in Fig. 5. Such a mechanism leads to lower melt temperatures and shorter residence times than those in screw extruders. In addition, a potentially more efficient "dissipative-mixmelting" mechanism (1) is also obtained.

Devolatilization

In the last elementary step, that of stripping and devolatilization, the advantages of a geometrical configuration of two moving plates are apparent. By placing a knife-spreader in the forward portion of the processing chamber, as shown in Fig. 6, the polymer melt can be spread into a thin melt film (with conveniently controllable thickness), on both disc surfaces; venting is then achieved through a vent port, and finally by generating a melt pool at the discharge end of the processing chamber, pressure is built up to pump the melt through a die or into a subsequent chamber. The subsequent chamber may be an additional devolatilizing chamber or a processing chamber performing another elementary step, such as mixing or pumping. It should be noted that in a stage-wise arrangement of devolatilizing chambers no backmixing takes place, thereby, greatly improving the efficiency of the process.

Out of the above description it becomes evident that the DISKPACK Processor configuration enables optimization of each individual elementary step and combines them into one optimal polymer processing system tailored to a specific need.

SCHEMATIC DISKPACK PROCESSOR DESIGNS

Depending on the particular requirements, a DISKPACK Processor can be built up out of one or more process chambers for each elementary step. The overall design configuration that evolves, therefore, consists of a pack of processing chambers in specific combination mounted on a single shaft. The polymer is being transferred from one chamber, or group of chambers, performing a given task to the next. By carefully selecting the number of chambers for each elementary step, the sequence of the steps and the operating conditions, the design can be tailored to processing needs. This process is demonstrated by the following examples.

Melt Pumping DISKPACK

A simple melt pumping DISKPACK is an obvious application of the processor in the post-reactor field. It involves a single elementary step, namely that of pressurization. Melt emerging from a reactor must be pressurized and pumped across a pelletizing plate. Presently short screw extruders and gear pumps are used for this application. Fig. 7 shows a schematic single stage DISKPACK pump design.

Experimental results clearly demonstrate the outstanding pumping capacity of the DISKPACK Processor in this configuration, its low power consumption and minimal temperature rise. Table 1 shows typical design information for single stage melt pumps of different production capacities. Depending on the inlet feed pressure, one or more feed-in chambers can be used in parallel to assure a polymer take-away capacity at the required rate. Fig. 8 shows such a design: the first stage has relative wide chambers that can be gravitationally fed. They will generate sufficient discharge pressure to force feed the melt into the narrow second stage chambers. Fig. 9 shows an alternative two-stage pump, where the feed chambers are flanking the central pump channels. In this configuration, external seals are exposed only to low pressure. This design is identical to a 350 mm diameter prototype melt pump which has been used for experimentation in our laboratory (Fig. 10)

Polymer melt is fed gravitationally through a large rectangular feed port exposing the four processing channels. Gravitational flow into the wide feed-in chamber is aided by an undercut in the barrel of an optimized design to assure maximum pressure flow generation. The melt in the wide chamber is pressurized while it is being dragged towards a helical channel cut into the barrel into the narrow chamber (5). The transfer of the melt from the wide to the narrow chamber is aided by drag exerted by the exposed disc top which forms one of the walls of the helical channel and which also provides for a self-cleaning action. The melt, subsequent to entering the narrow chambers, is exposed once again to the inlet port and then dragged toward the channel blocks with a linear buildup of high pressure needed for pelletizing. Table 2 shows the simulated effect of disc speed on flow rate for a 350 mm 2-stage LDPE pump, as well as the disc speeds and diameter for two large capacity pumps.

The compactness and effectiveness of the DISKPACK melt pump is comparable to gear pumps. But, unlike gear pumps, polymer degradation is expected to be minimal and there is no danger for machine damage by foreign objects.

Stripping DISKPACK

A schematic design configuration for a stripper or devolatilizer is shown in Fig. 11. In this design seven stripping chambers are flanked by a wide low pressure inlet chamber to accept low pressure molten feed, and a narrow wedge-shaped high pressure chamber at the discharge end for pumping. The total number of stripping chambers is set by processing needs, and the type of volatiles. It includes both stripping reactor products from solvents and unreacted monomer (desolventization), as well as the common post reactor devolatilization step where traces of low molecular weight contaminants are removed from the polymer. When large amounts of volatiles are present, convective mass transfer occurs by a mechanism of bubble transport. At low volatile content, however, the process is characterized by diffusion controlled mass transfer in a viscous medium where the key elements of an efficient removal mechanism involve a repeated process of (a) spreading the viscous solution into a thin film with large surface area, (b) exposing the surface to low partial pressures to attain low surface equilibrium concentration, and (c) mixing the film after relatively short exposure times when diffusion rates quickly diminish.

In the stripping chamber the viscous liquid can be conveniently spread into a thin film on the disc surfaces by a spreader attached to the barrel in the inlet region of the processing chamber. A vent in the barrel exposes the film to vacuum, and finally the melt pool that collects at the discharge end performs the two functions of mixing and generating pressure to pump the liquid into the subsequent stage where the above process is repeated. The chamber widths are small and many chambers, creating large surface areas, can be packed into small volumes.

It is worthwhile to note that the stage-wise forward moving nature of the process leads to a unique advantage over other machines, in that no back mixing occurs, resulting into a high overall mass transfer efficiency. A stripping DISKPACK Processor has, therefore, an excellent potential for effective devolatilization, meeting the ever increasingly stringent purity requirement of polymeric products.

Plasticating DISKPACK

For those polymers emerging from the reactor in solid form, the first elementary steps required are solids handling, conveying and melting (plastication) before other elementary steps, like mixing, devolatilizing and pumping, can take place.

Figures 12, 13, and 14, show, respectively, schematic designs of a melter (plasticator), melter-pump combination, and a "total" processor or plasticating DISKPACK consisting of melting, devolatilizing, mixing and pumping chambers. The parallel melting chambers can generate sufficient pressure to feed into an appropriate die. This is a simple and useful configuration, in particular since experiments indicate that substantial mixing also takes place in a solids-filled chamber where melting occurs. If, however, the pressure so generated is insufficient, the molten polymer can be channeled toward a high pressure pumping chamber, as in Fig. 13. A particular advantage of this design configuration is that sealing requirements are restricted primarily to solids filled, relatively low pressure, outboard chambers. Finally, a "total" processor or plasticating DISKPACK schematic design configuration is shown in Fig. 14. The sequence of the devolatilizing and mixing steps is set by process requirements and may be reversed. Similarly, the number of chambers pertaining to any of the elementary steps is determined by processing needs.

Clearly, such a DISKPACK Processor can carry out all the five elementary steps to meet the process requirements of the user.

OTHER FIELDS OF APPLICATION

The potential fields of application of the DISKPACK Processor embrace many other phases in polymer processing than the post-reactor application already described in detail.

Starting upstream with polymerization, theoretical considerations suggest that the DISKPACK geometry offers some unique advantages as a continuous polymerization reactor. By appropriate design of the individual processing chambers, a broad range of viscosities can be handled and the processing chamber can be designed to perform similarly to continuous stirred tank reactors or plug flow reactors. By operating with controlled recycle, a DISKPACK reactor chamber can operate anywhere between the extremes of the two types of reactors. Furthermore, by selecting an appropriate parallel and serial design configuration of processing chambers, the residence time in the various stages of polymerization can be controlled. Initiator, chain transfer agents and other additives can be added in optimal sequence. Good temperature control can be obtained using a hollow disc design with liquid circulation. It is feasible to recycle the reactants from an advanced state of polymerization to an initial stage, thus aiding or eliminating the need to handle the very low viscosity monomeric liquid. Moreover, the plug type flow attainable in the advanced stages of polymerization has significant advantages in both a chain and a step type polymerization reaction in achieving narrow molecular weight distribution.

Polymerization can be followed on the same shaft, or in a separate DISKPACK unit, by the stripping operation. Chamber design will allow the feeding of solutions with a medium to high solids content.

Downstream from the post-reactor processing operation, other fields of application are color compounding and precision extrusion, both based on the "total" processor design concepts (Fig. 14).

Also in the field of synthetic rubber processing, the DISKPACK will find several immediate applications: that of stripping directly after the reactor and the compounding of powdered and liquid rubbers in combination with the shape extruder step.

EXPERIMENTAL RESULTS

A 7.5" diameter single chamber DISKPACK Processor has been used for all the initial experimental development work. With different chamber designs, melt pumping, plasticating and mixing experiments were completed for various polymers and results were compared with the predictions according to the theoretical models. In general a close relation has been found between those two values.

More recent test work took place on a two stage 7.5" diameter processor for similar experimentation and the usage of two commercial prototype machines: a 350 mm diameter melt pump DISKPACK (see Fig. 9, 10) and a 350 mm "Total" Processor described in further detail hereunder.

Experimental data on these machines will be disclosed when this paper is presented in public.

DESIGN OF A 350 MM DIAMETER 15 CHAMBER PLASTICATING DISKPACK

On the basis of theoretical simulations and experimental findings (1) the first plasticating DISKPACK has been designed and built. Specifically, the processor was designed for studying the DISKPACK performance in the fields of (a) post-reactor processing for polymers emerging in solid form from the reactor (e.g. PP, HDPE) and (b) precision extrusion of various polymers. A target production rate of 1,500 lbs./hr. (680 kg/h) of PP was set. For post-reactor processing, this production rate represents pilot plant scale, whereas, for precision extrusion it represents a full scale machine. The design process resulted in the 350 mm (13.9 in.) diameter, 15 chamber machine shown in Picture 1. The machine is located at the DISKPACK Laboratory facilities of the Farrel Company.

The first phase of the design process was the definition of the overall processor configuration. The schematic design configuration in Fig. 14 was selected. This design configuration, has two key advantages: (a) the high pressure chambers are in the center of the machine flanked by solids filled low pressure chambers at the outboard simplifying seal design, (b) optimal matching of pump and melting chamber design requirements can be obtained by having the molten streams from both symmetrical sides of the machine converge into a single pump.

Simulation studies of melting performance, coupled with manufacturing consideration, led to the selection of 350 mm diameter discs and 10 melting chambers. Therefore, a pack of 5 chambers, fed by solids in parallel, was placed on either side of the machine.

The extrudate from each pack of chambers is collected into a common transfer channel and fed in series into a single mixing chamber followed by a devolatilizing chamber. Both streams then converge in a central pump. The pump is designed to generate 1500 PSI (102 atm) pressure. The geometry of the chambers was optimized for their particular function, keeping in mind compatibility requirements of the consecutive stages.

A number of design points of special interest are worthwhile to note and discuss.

Key to the successful application of the DISKPACK concept to processing machines is the efficient transfer of the melt from stage to stage at low pressure losses and without stagnant regions. This is obtained by the previously described "internal" transfer channels where the disc top drags the melt forward to the next processing chamber. All transfer channels and channel blocks are located on rectangular plates which fit into similar sized slots in the barrel.

By removing these plates, all key elements of the machine are exposed, and machine modifications and adjustments simplified.

Turning next, briefly, to the sealing requirements, it should first be noted that these are different for outboard chambers than for internal chambers. Whereas the former requires preferably zero leakage, substantial interchamber leakage can be tolerated. Both, however, involve in principle sealing a rotating element containing a pressurized viscous liquid. Fortunately, a number of engineering solutions are available, some of which can take advantage of the non-uniform angular pressure distribution in the processing chamber. Thus, an observer located on the disc top (where sealing is to be achieved) experiences a "sawtooth" type pressure trace, rather than a continuous pressure level.

Closely related to sealing considerations, as well as conventional machine design considerations, is shaft deflection stemming from the above mentioned angular pressure profile. To reduce shaft deflection to a minimum and, therefore, a low bearing load, the channel blades are not located on a single transfer plate but several transfer plates placed in opposite angular positions to balance forces.

For an effective disc temperature control system, a circulating liquid (oil) system was selected. Two independent temperature control regions were incorporated into the design. The liquid transfer channel size and configuration was carefully designed to allow ample flow rate of the temperature control liquid to maintain a low temperature difference between inlet and outlet, and to provide for a sufficiently high heat transfer coefficient on the disc surfaces to meet the specific thermal load requirements.

Reference List:

1. Z. Tadmor and C. G. Gogos: "Principles of Polymer Processing". Wiley, New York, 1979.
2. M. Gray, British Patent 5056, 1879.
3. Z. Tadmor, P. Hold, and L. Valsamis, "A Novel Polymer Processing Machine, Theory And Experimental Results", presented at SPE, 37th ANTEC, New Orleans, 1979.
4. Z. Tadmor, "Method and Apparatus For Processing Polymeric Materials" - Patents to be issued.
5. Z. Tadmor, P. Hold, and L. Valsamis, "Method And Apparatus For Processing Polymeric Materials", Patent applications for Farrel Company pending.
6. Z. Tadmor and I. Klein, "Engineering Principles Of Plasticating Extrusion", Van Nostrand Reinhold Book Company, New York 1970.
7. P. Hold, Z. Tadmor and L. Valsamis, "Applications And Design Of The DISKPACK Polymer Processor" - paper presented at the 37th Annual Technical Conference, Society of Plastics Engineers, New Orleans 1979.

TABLE I

Single stage melt pump designs for various production rates
for LDPE with 1500 psi discharge pressure.

Output (lb./hr.)	Disc Dia. (in)	Disc Gap Separation (1) (in)	Disc Speed (RPM)	Temp Rise (2) (°F.)	Shaft Power (3) (HP)	Specific Power (HP/lb/hr.)
1,000	10	.20	91	5	4	.004
5,000	20	.40	63	6	19	.0038
10,000	25	.45	63	4	34	.0034
25,000	35	.60	60	4	87	.0034
50,000	45	.80	56	4	172	.0034

- (1) At the outside diameter of a wedge-shaped chamber.
- (2) Adiabatic
- (3) Excluding power dissipated over channel block; disc tops and seals.

TABLE 2

Two stage double chamber melt pump designs for various production rates for LDPE with 1500 psi discharge pressure.

Output (lb./hr)	Disc Dia. (in)	Disc Speed (RPM)
1,500	13.8 (350mm)	32
5,000	13.8	83
25,000	30.0	49
50,000	40.0	46

SPECTRUM OF PRODUCTION

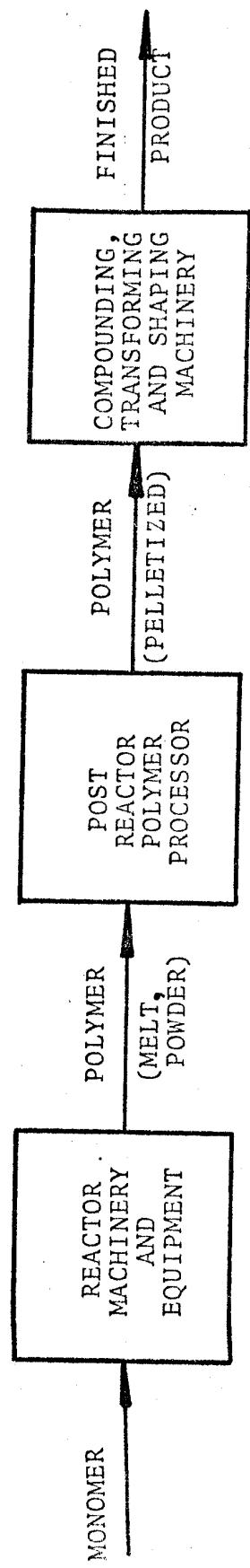
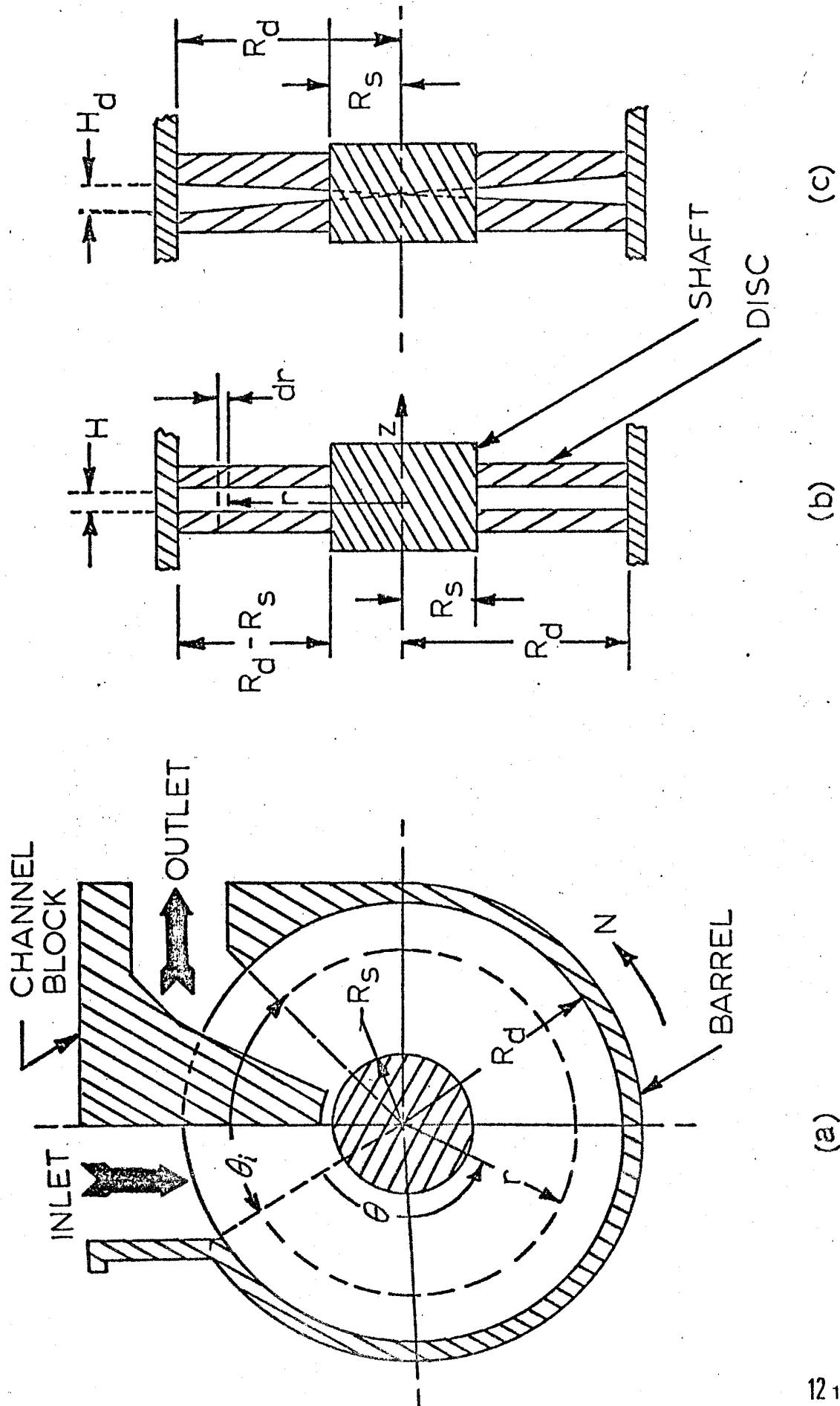


FIGURE 1

FIGURE 2



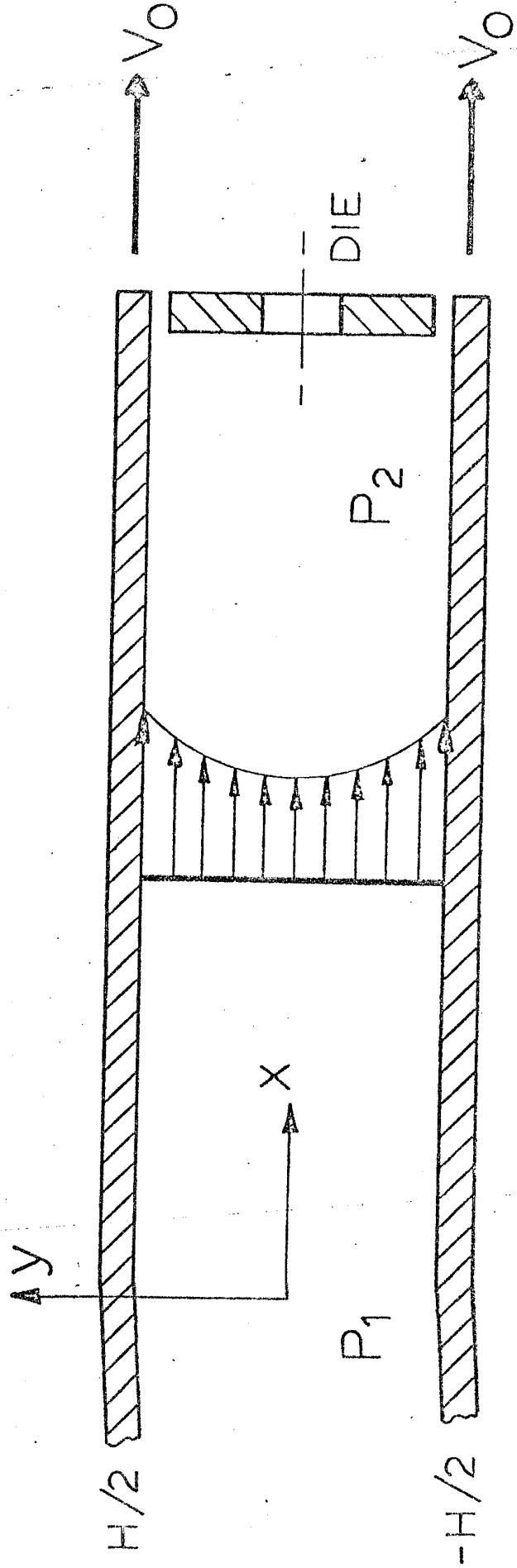


Figure 3

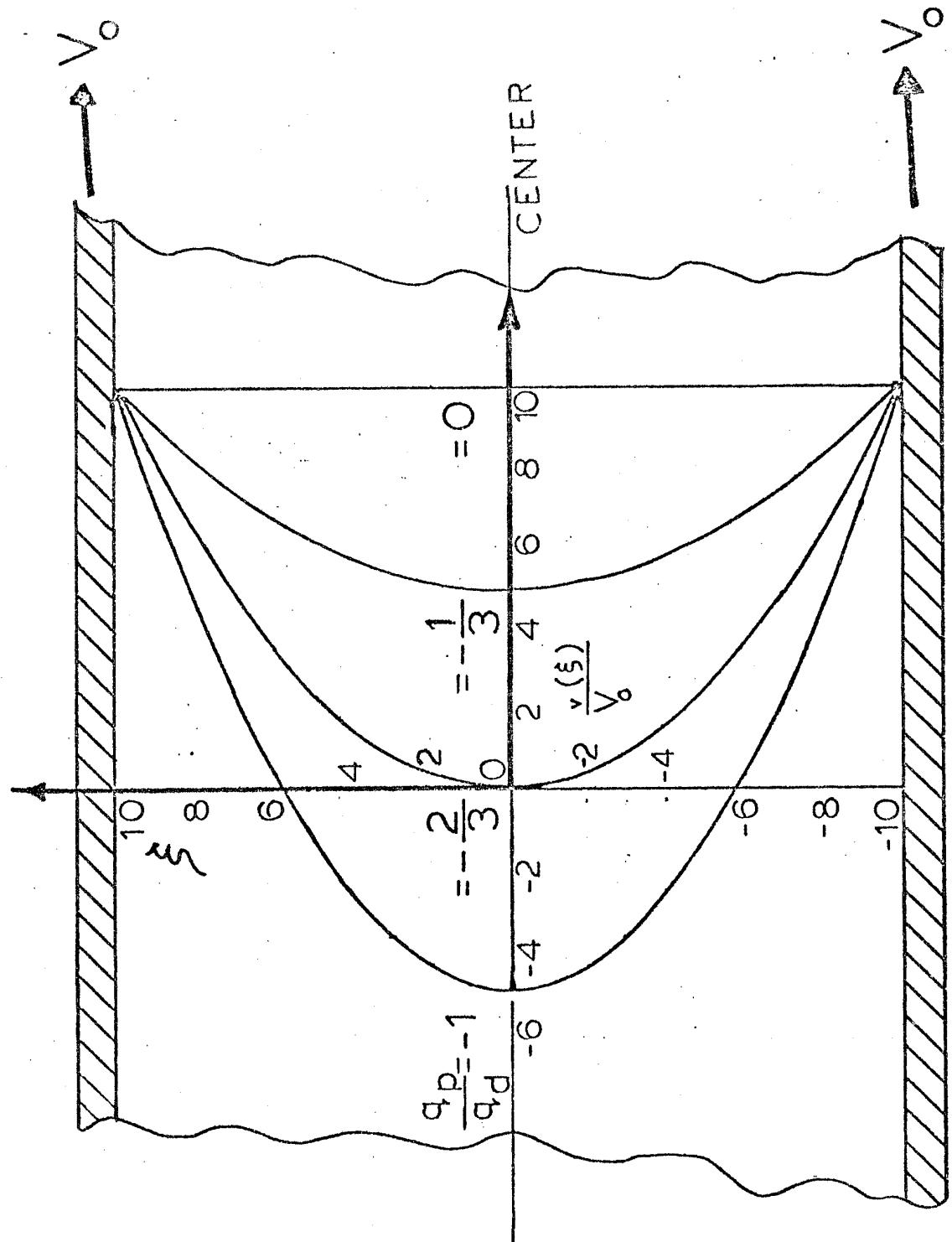


FIGURE 4

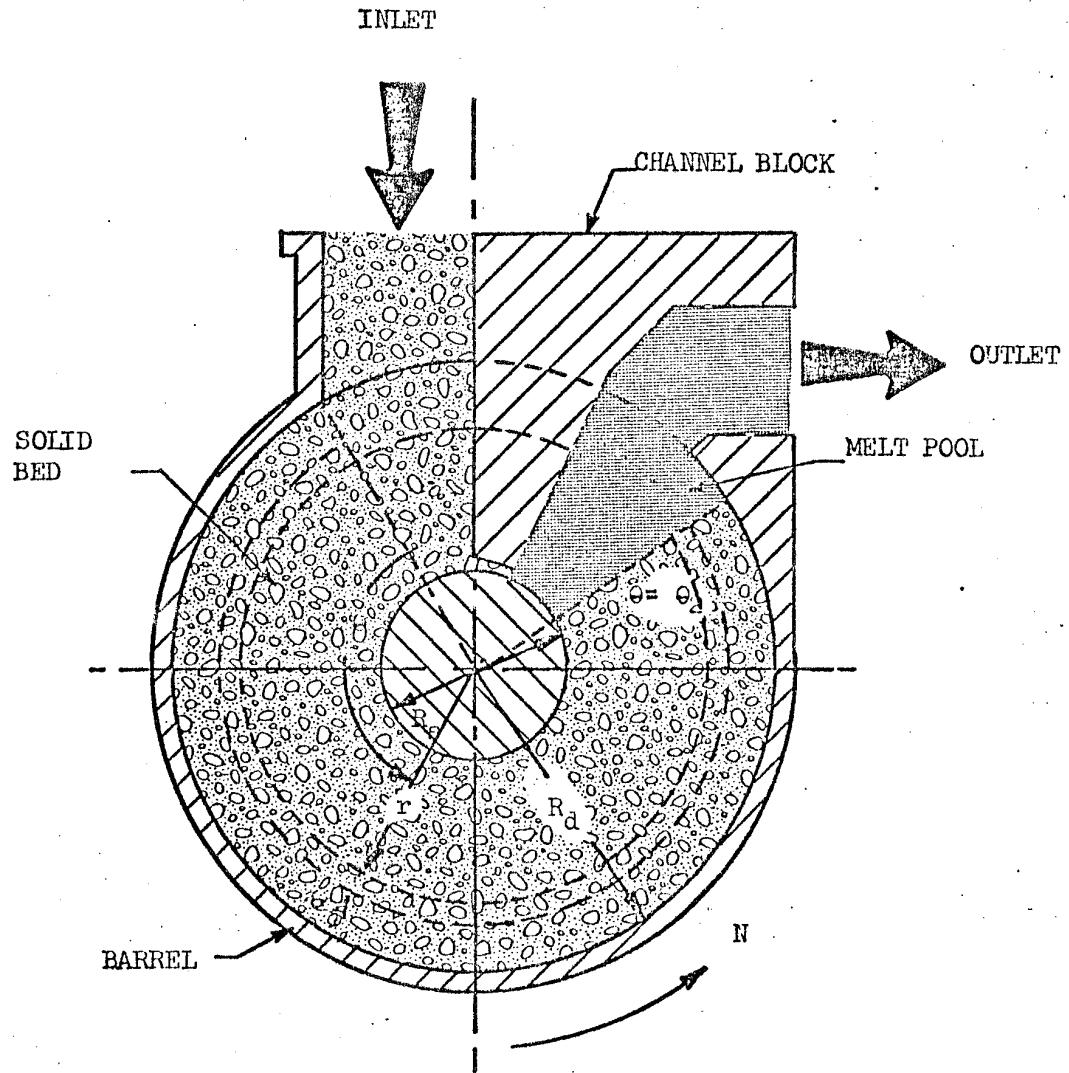


Figure 5a

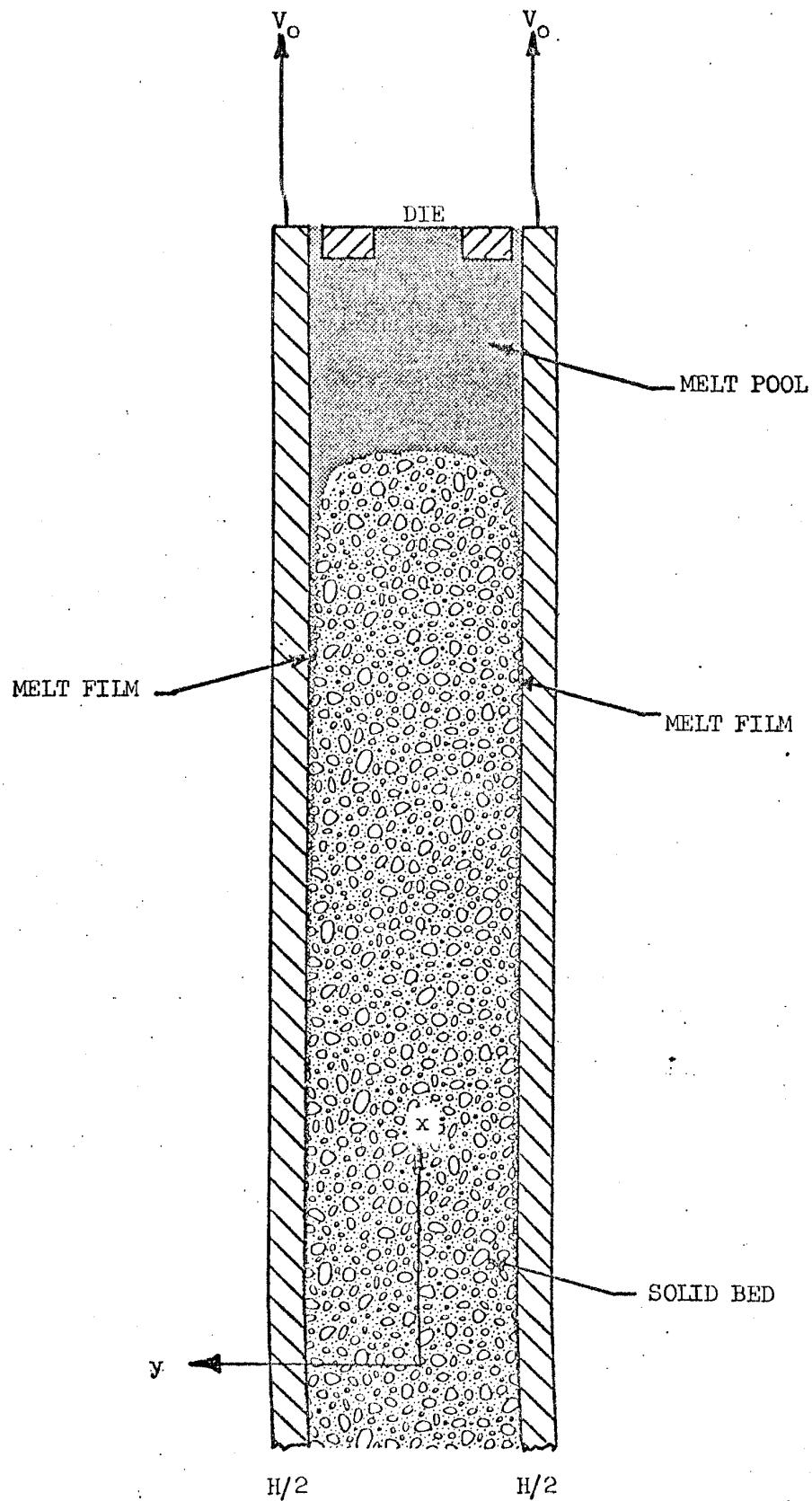


Figure 5b

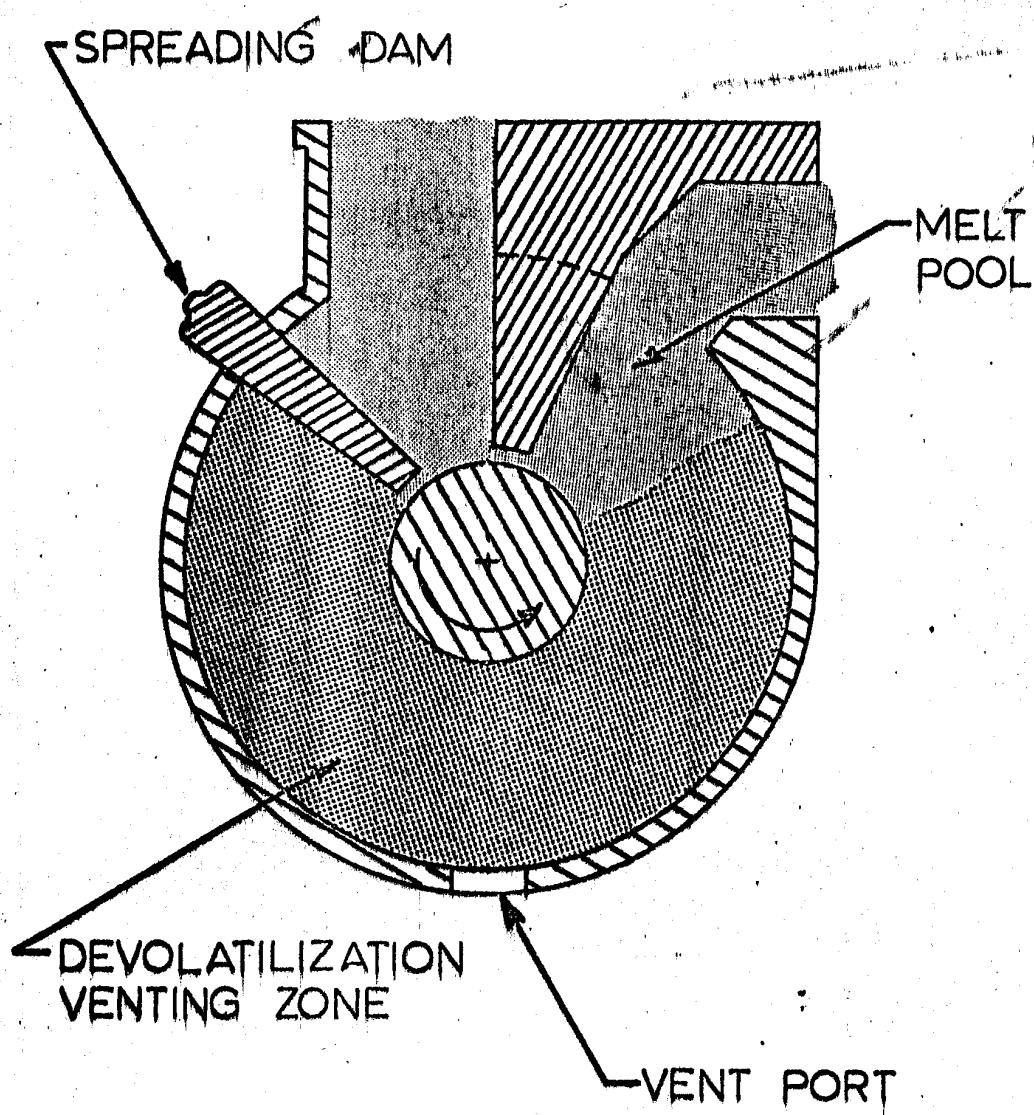
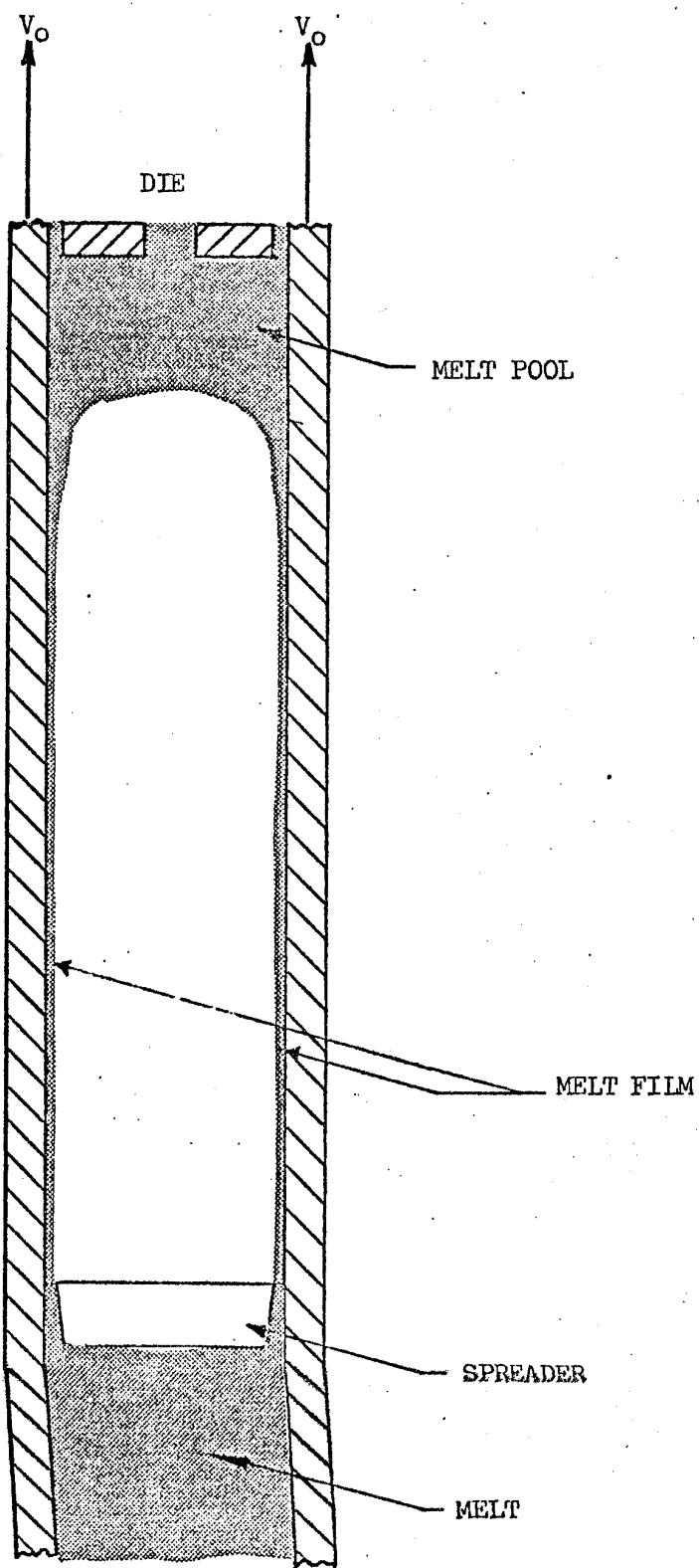


FIGURE 6a



12 24

Figure 6b

SINGLE STAGE PUMP

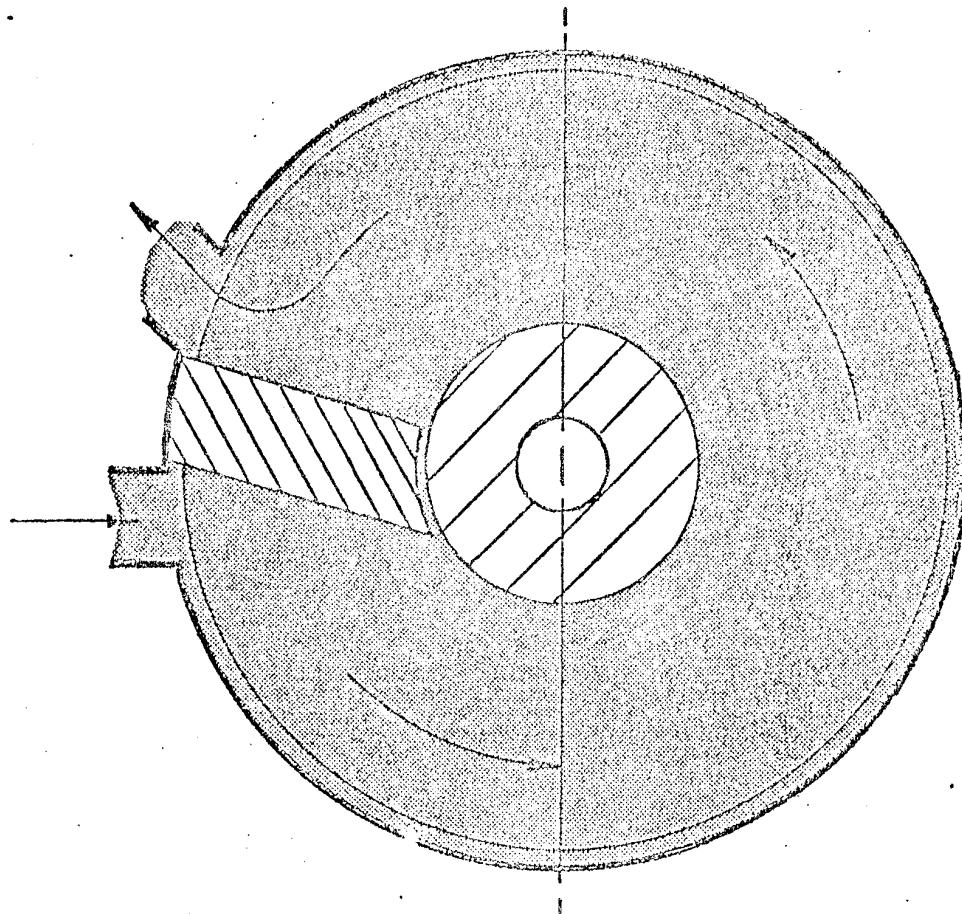
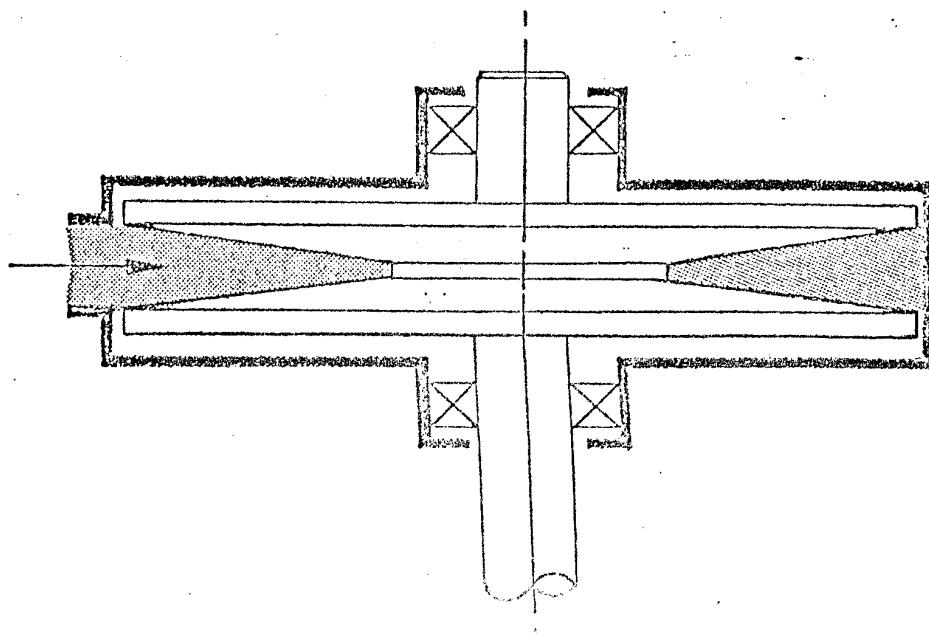


FIG.7



1225

TWO STAGE PUMP

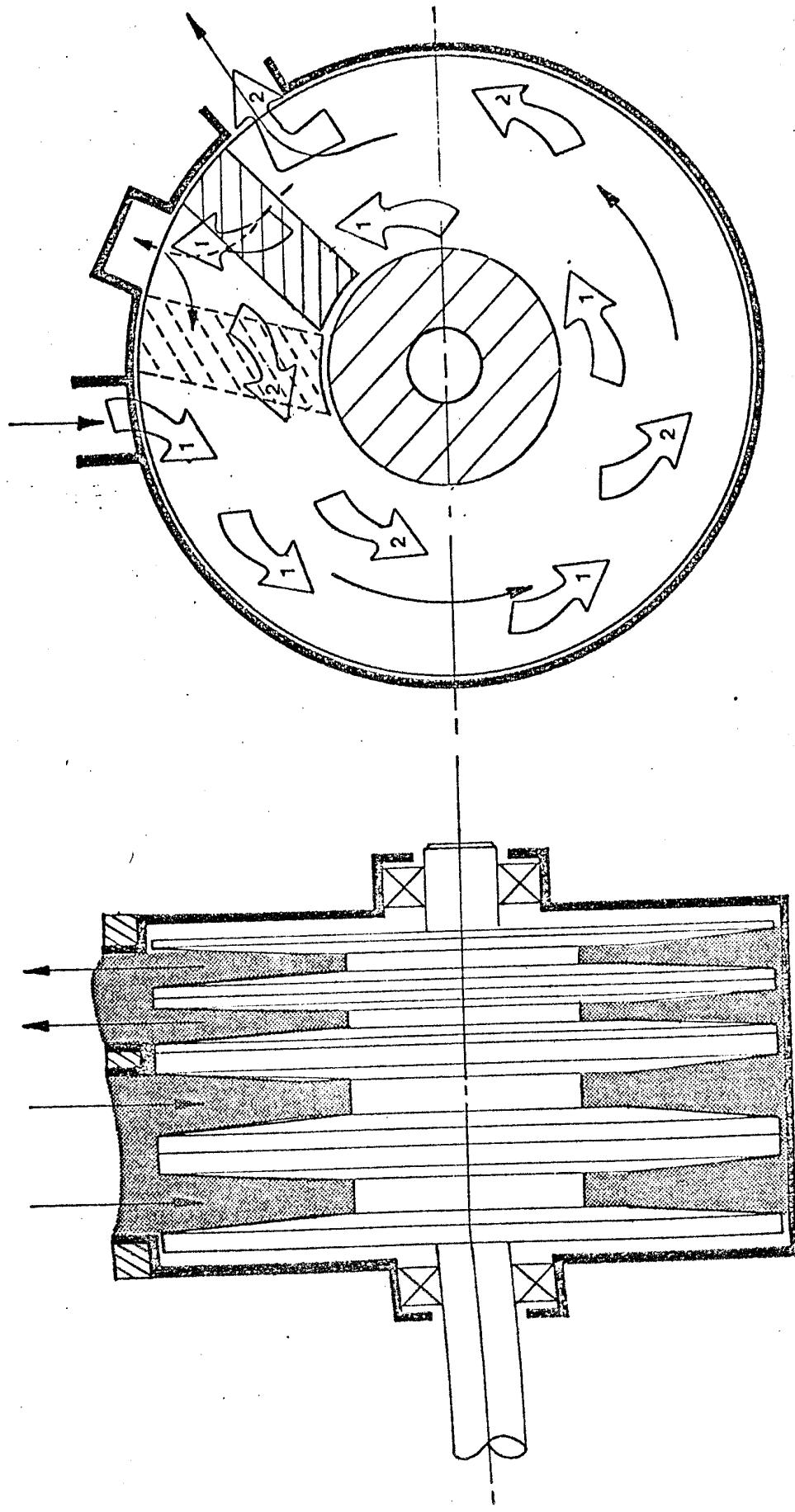


FIG. 8

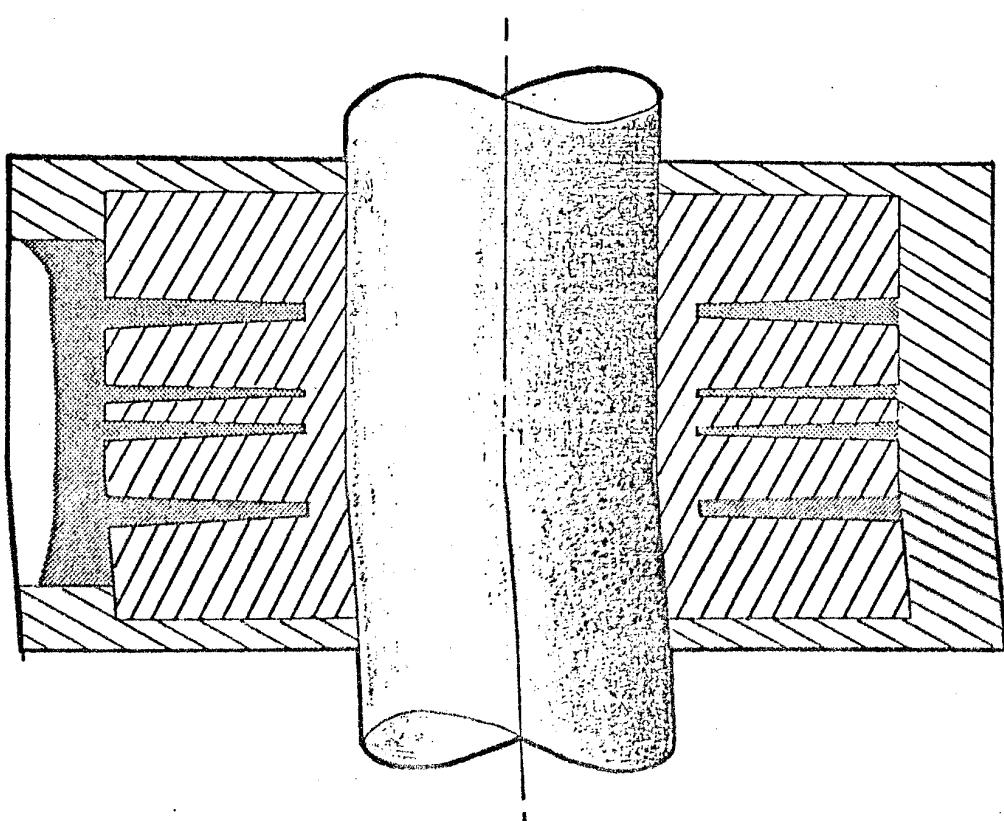
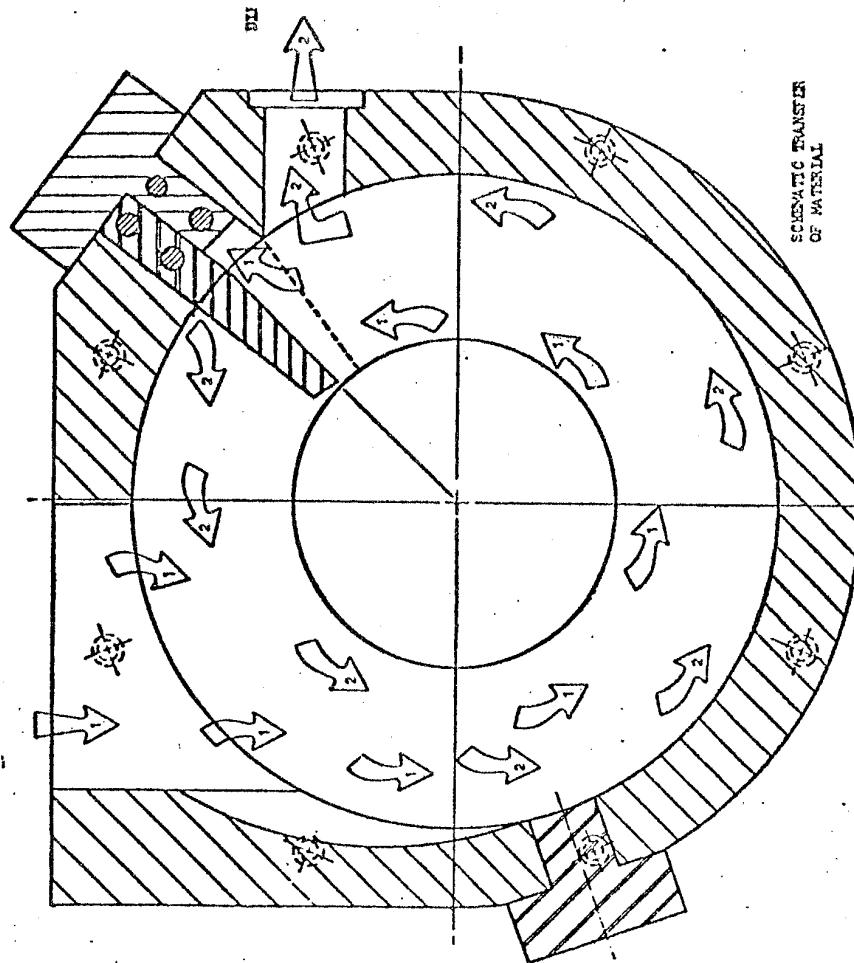


FIG. 9.

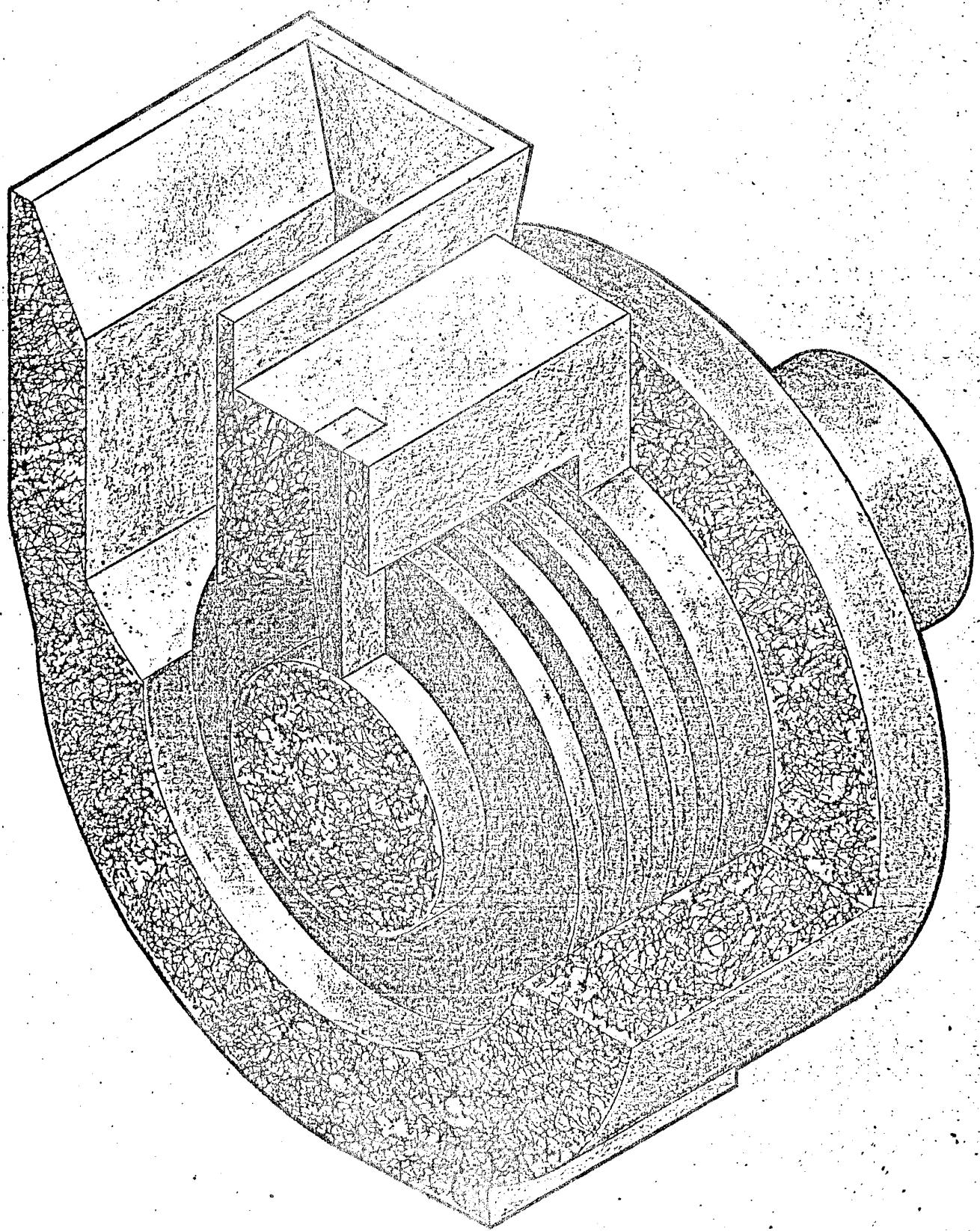
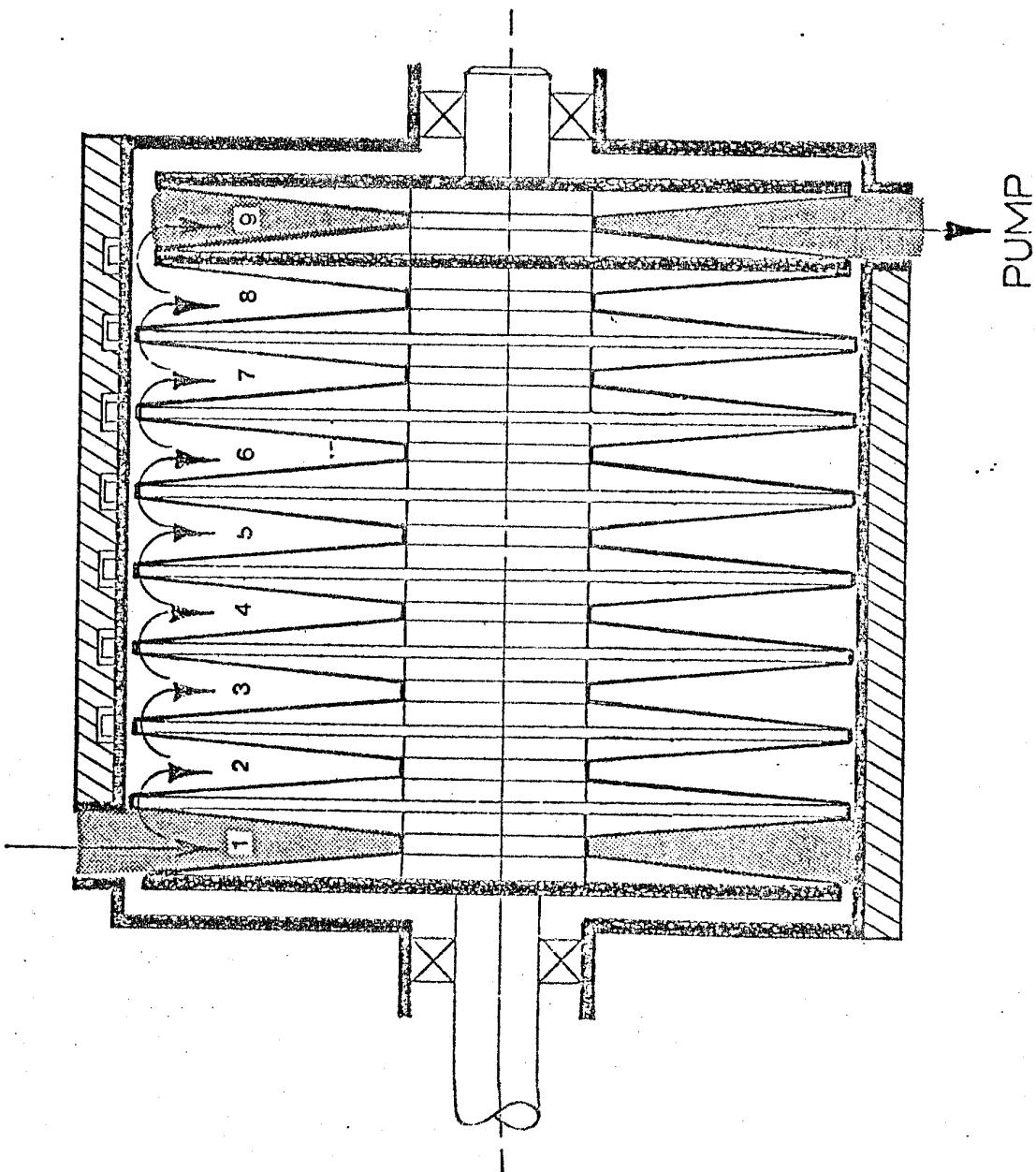


FIG.10

12 28

FIG.11



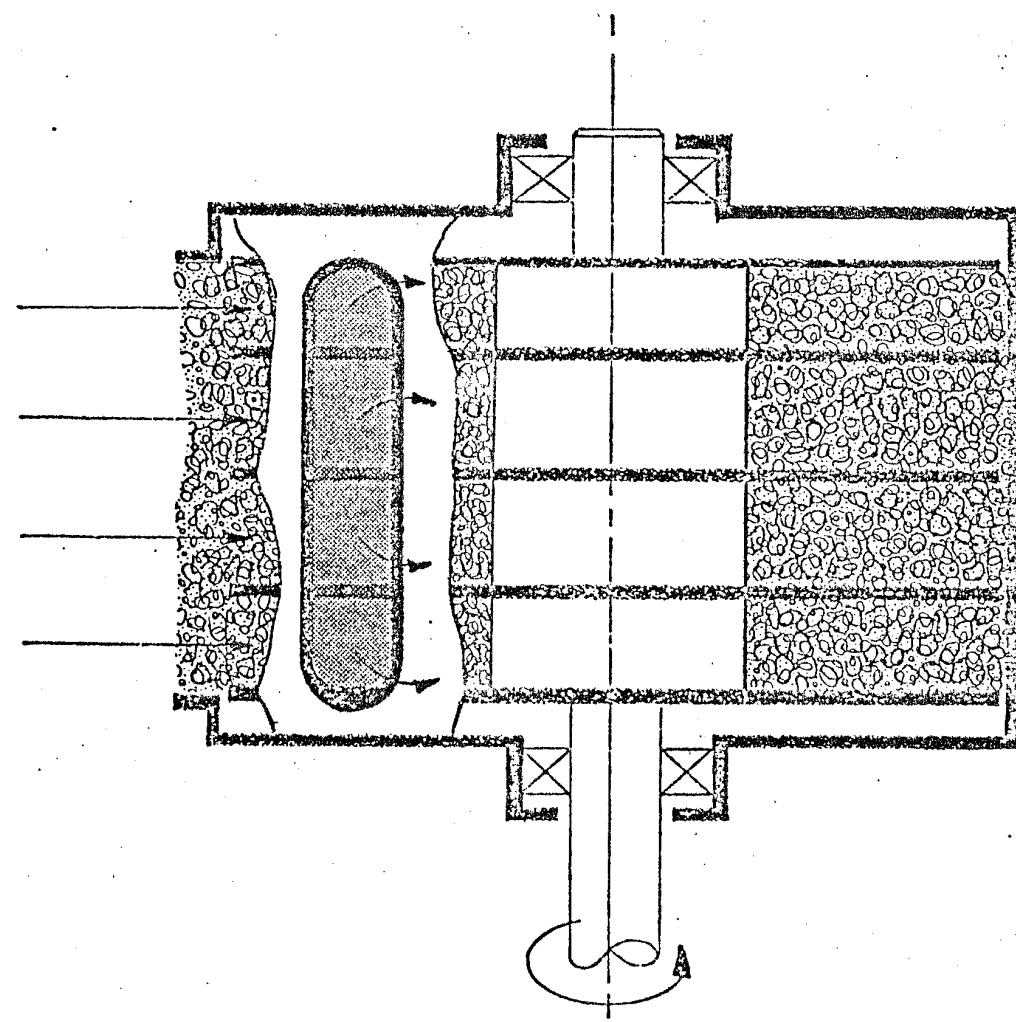
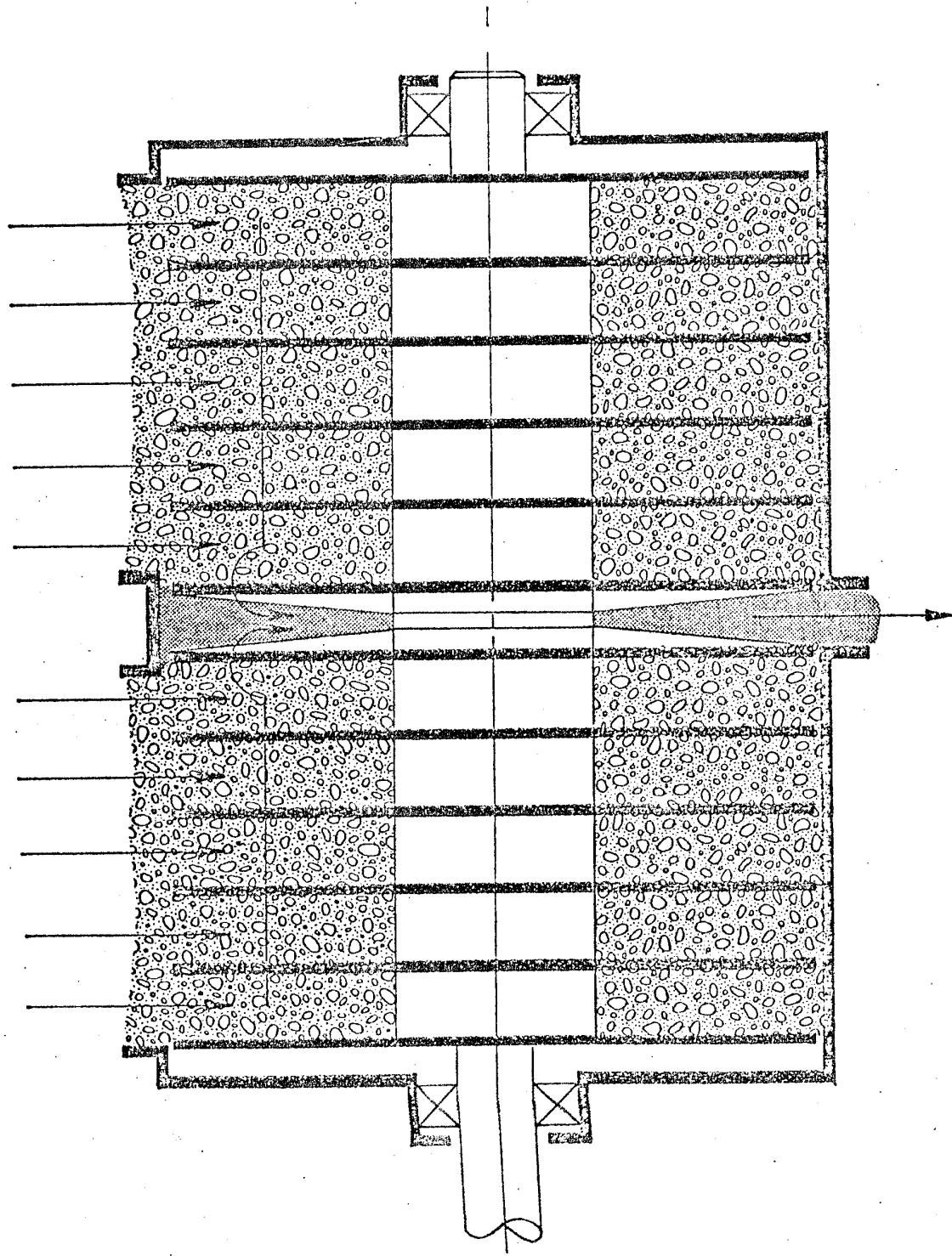
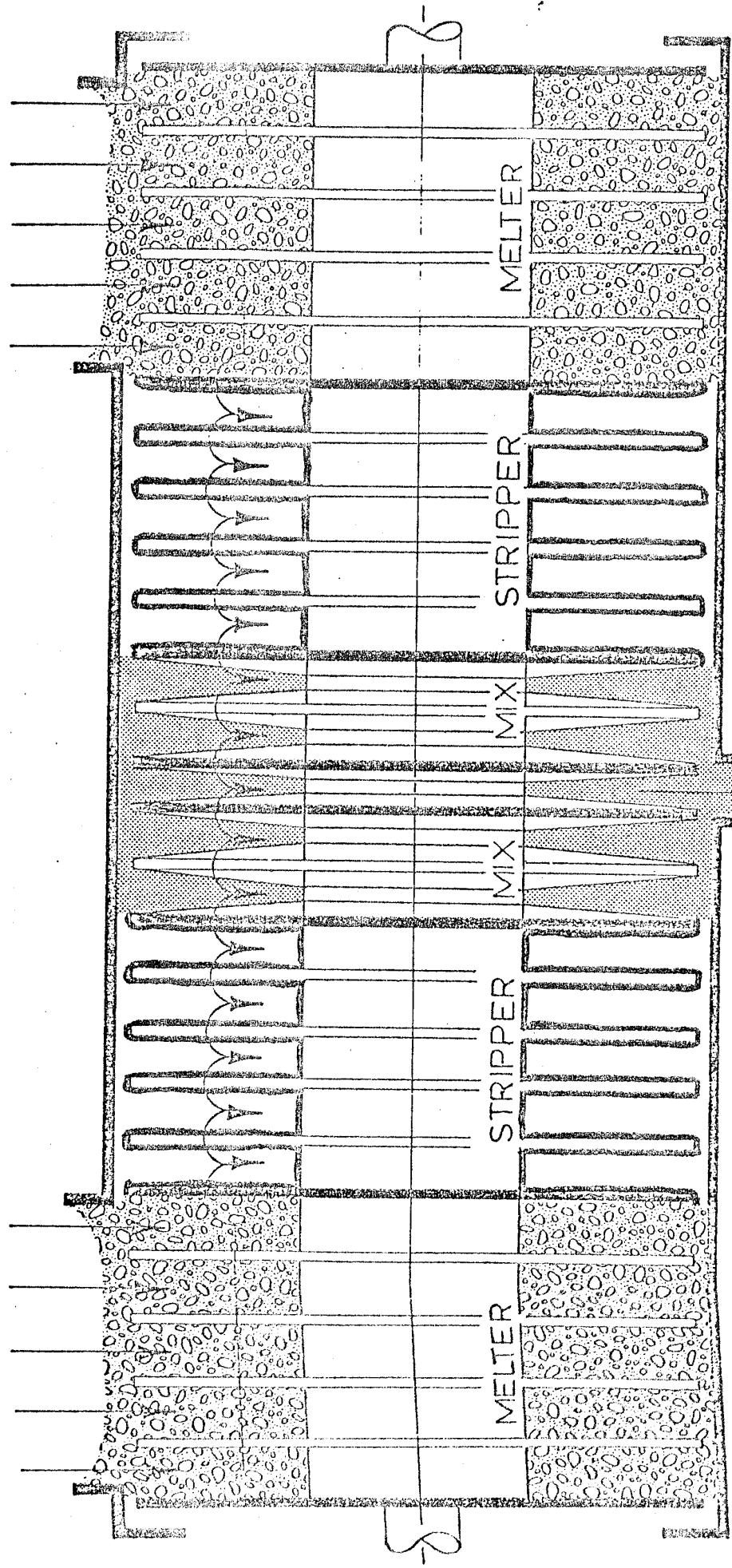


FIG 12

FIG.13





SOCIETY OF PLASTICS ENGINEERS

First EURETEC

Gent, June 14 - 15, 1979

Friday

Afj

(Note: the English is
atrocious, but there is a
lot of good info here!)

CROSS-LINKING OF HIGH DENSITY POLYETHYLENE

J. TERRISSE

I - INTRODUCTION

Polyethylene, one of the oldest plastic material is still the most used today because his specific and very variable physical properties.

The present trend in research which tends to spread out the use of common plastics by improving their properties by special processes has been an efficient ground for the development of Cross Linked PE.

The main interest, indeed of this plastic is that at room temperature all his standard characteristics are preserved or ameliorated and at temperatures above the meeting of his crystalline phasis it appears as an elastomer. In fact we can consider Cross Linked PE as a naturally crystalline rubber.

Such a broad range of physical properties opens lots of application possibilities. But as we shall see later, processing difficulties make the product rather expensive. It can only replace his conventional rubbers or thermoplastics challengers for high quality technical products or if a high level of long term reliability is required.

So, it is not surprising that this material has been introduced in very technical applications as for example, wire coating and in the electrical engeneering as shrinkable sleeves, in building for hot water supply. But still for much common use Cross Linked PE has his interest for skin pack and foams for example.

Wire insulation and shrinkable films or sleeves are the main issue today with approximatly 18 000 tons years for wires in France for example more or less in Germany and Italy or 3 000 tons hot water pipes are produced in Germany. Both markets have a strong growth rate.

As far as processes are concerned three cross linking technics are used today.

- 1) The peroxyde cross linking which occurs at high temperature. This process is used for LDPE cross linking for wire and HDPE for pipes.

- 2) Vinylsilane grafting on to the carbone backbone followed by hydrolysis in the solid state. This process is used for wires and pipes too.
- 3) High energy irradiation (β or γ) leads also to cross-linked materials. This process is used preferably for thin products but nevertheless cross-linked PE pipes and special kind of wires can be produced by this way.

II - We shall now very briefly relate these different cross linking way.

1) The peroxyde way :

At relatively high temperature peroxydes such as Dicumyl peroxyde, ditertiobutyl peroxydes and a lot of such compounds decomposes. As the main reaction, in two radicals which react with the PE backbone, both radicals relieves each one an hydrogene, forming two macroradicals. These two again react forming a cross linked point with four branches.

In fact the reaction is much more complicated and depending on the peroxyde used a lot of side reactions are possible. These reactions, sometimes, can be the occasion of severe troubles, as bubble forming. One must keep in mind that before cross linking the macro radical can decompose in two chains, specially near a branching. So, cross linking is a competitive process between chain cutting and linking. The highest linking efficiency is obtained with linear products as shown in the figure.1

On the other hand it is clear that for a given cross linking points density, the main chains will be the better linked, the longer the original chain length is. The average chain length between two cross linking points is called M_c . The shorter M_c the tighter the network and the product will have at high temperature (150°) the properties of a strong elastomer.

From the initial viscous state of the melt to the high elastic and

ρ PE	% W	% A.O.	Rad.EFF.	n	Nature
0,924	1.5	0.16	0.71	0.82	Ditertiobutyl. perox.
0,960	1	0.11	1.6	1.06	"
0,924	2.8	0.16	0.66	0.90	Dicumyl. perox.

(After Köhnlein)

FIG 1

and product, one can observe a continuous variation of the viscoelastic properties of the material as the number of chains fixed in the network increases.

The cross linked chains are no more soluble but in toluene or other aromatic compounds, the network swells. The extend of this swelling is also a measurement of the compactness of the network -in other words of the length of M_n .

2)- High energy irradiation way

An other way for cross linking PE is the irradiation with high energy rays. The most used are electron of 0,5 to 4 MeV but X ray works too, even UV and X ray can be used.

The radiation leads to ions or several excited macromolecular species which can produce macroradicals. In the case of PE the macroradicals formed can react together giving a linking point. Each cross linking point gives one hydrogene molecule. There is however a important difference between peroxyde cross linking and irradiation process.

In practice the irradiation is carried out at temperatures around 40 - 60°C, in the solid state. Photons and electrons produce radicals in the crystalline and the amorphous phases ; but the mobility of the chains inside the crystals is too low for an efficient recombination and many radicals remain trapped waiting for another lonesome electron. Unfortunately, oxygen can satisfy very easily this need of electron by giving an hydroperoxyde. This kind of peroxyde is ineffective in cross linking, but very effective to break down at relatively low temperature and split the backbone in two chains. This phenomenon is more important in high crystalline PE and so called post-oxydation. It is more severe thinner the product is or the higher the radiation dose is too.

It is very difficult to avoid this phenomenon since it is not possible to protect the chains inside the crystals and in any way ever every stabilisation compound reduces the cross linking effectiveness in the amorphous phase.

In such a process if a high cross linking level is required, it is very useful to compound the PE with some polyfunctional monomers such as di or tri acrylates of glycols or for example triallycyannate. These compounds increase the cross linking effectiveness. Siemens

has patented a process in which the additives are grafted or homopolymerised by a very small peroxyde quantity in order to reduce or even eliminate the exudation of the additives before irradiation. So it became possible to raise the reactivity in such a maner that it is possible to stabilise and (or) réduce the required radiation dosis.

The silane Way

Still another process of cross linking consists in grafting, using a peroxyde, during the extrusion of a vinyl silane compound on to the PE backbone.

The process patented by Dow Corning use trimethoxyvinylsilane. This silane as it is well known reacts with water and a neighboring reactive group.

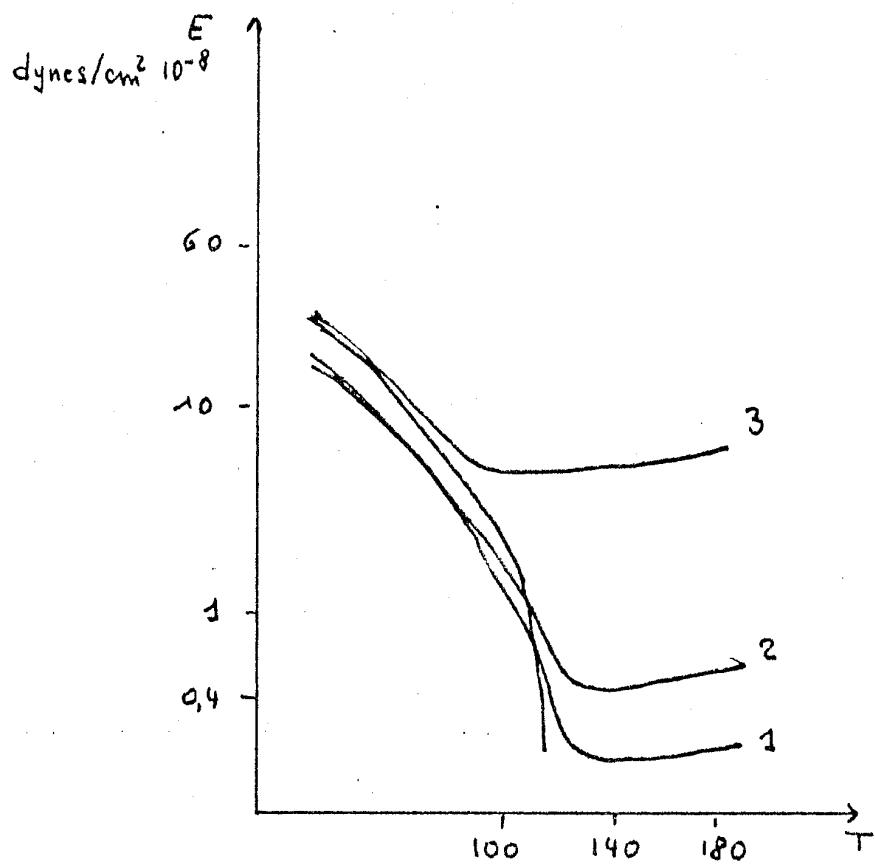
The grafting reaction is performed in an extruder on LDPE or HDPE. The hydrolysis catalysed with a tin compound occurs in the solid state after extrusion in a hot water reservoir or in a steam atmosphere by 50 - 100 or even 110°C for HDPE.

Once more for this cross linking process the linking points are produced in the amorphous phasis existing before hydrolysis and one or two methoxy functions can react theoretically, so the functionnality of the cross linking points can be higher than 4. But this is not well etablished.

III - Now we will rapidly examine the physical properties of this different kind of cross linked PE.

As mentioned before the main useful and original property of cross linked PE is its characteristics of cristalline elastomer. One can see on the figure the evolution of shear modulus versus temperature where curve 1 and 2 concern two HDPE of different cross linking level 2 as has a tighter network than 1.

Noteworthy is also the slow increase of the modulus after the melting point by increasing the temperature ; a typical property of elastomers. This property is of a particular interest in the wire insulation where

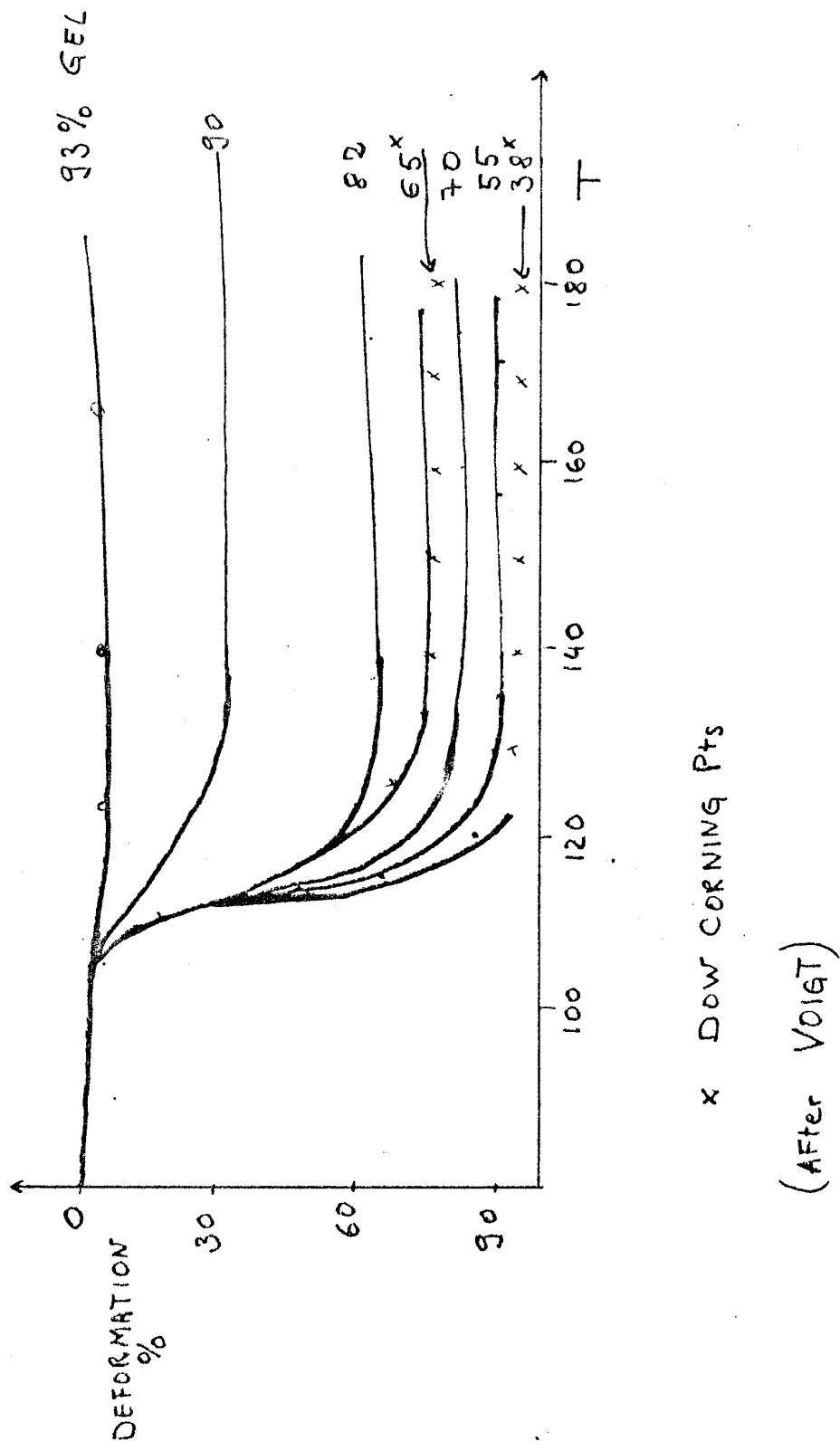


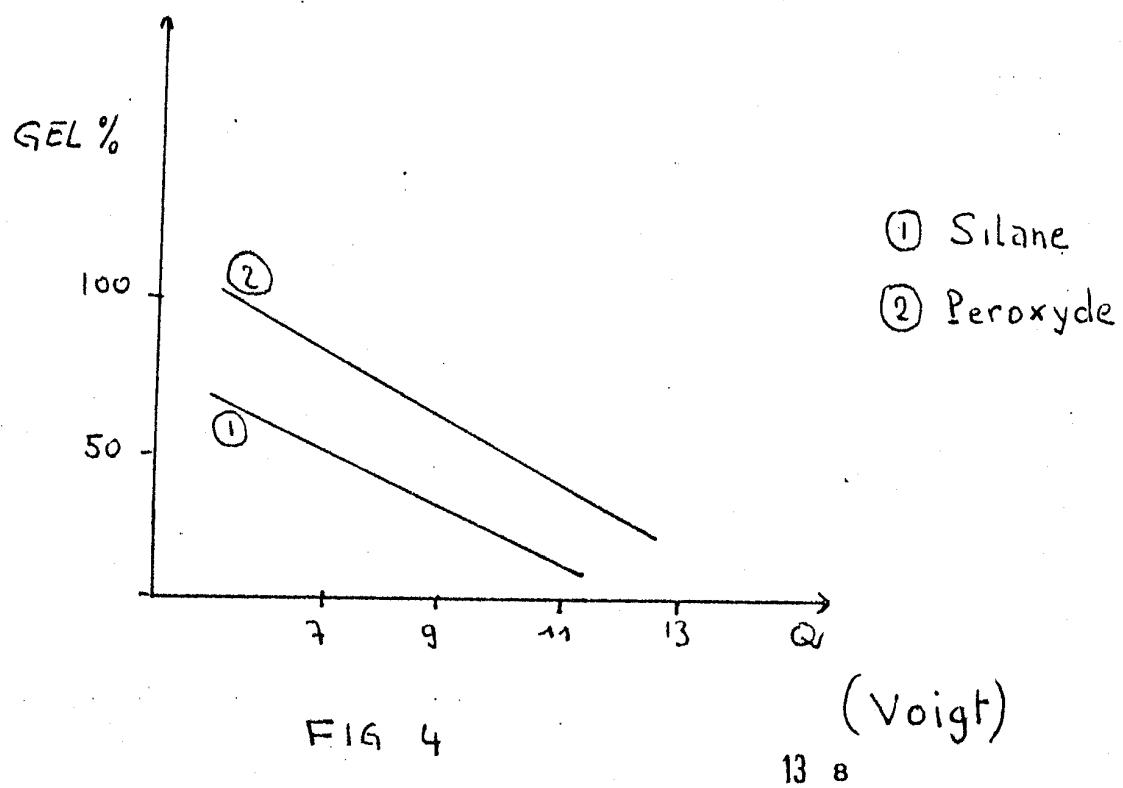
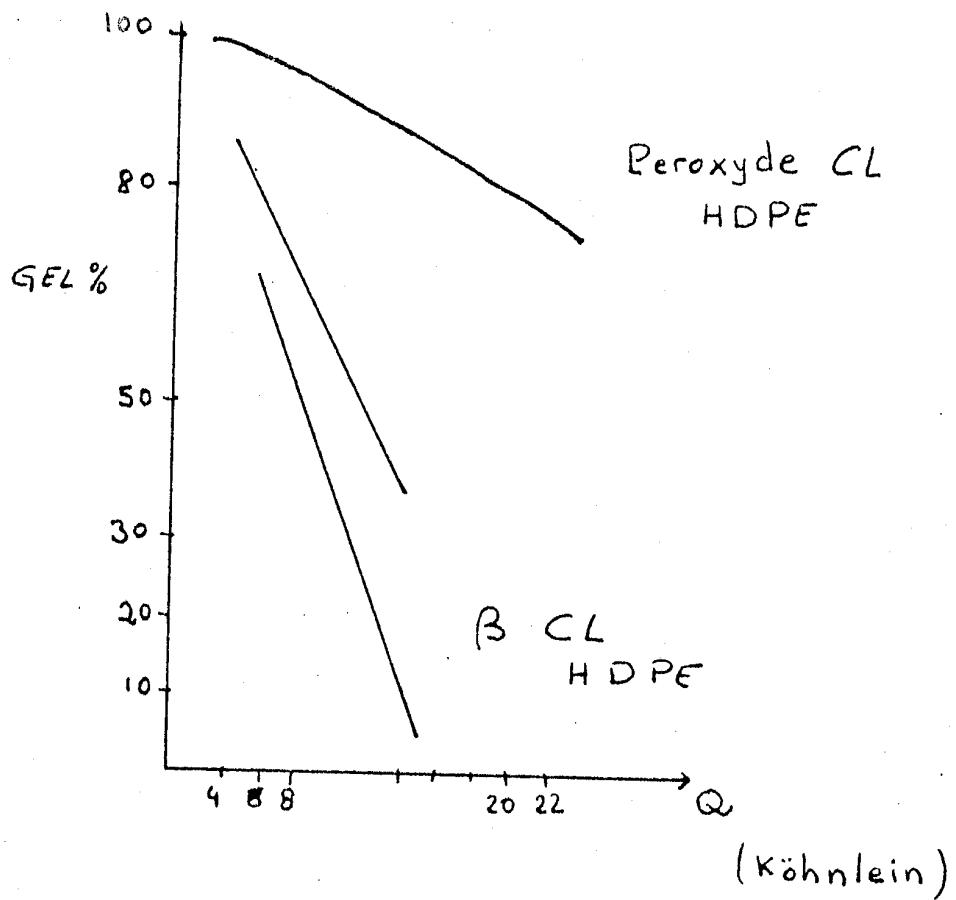
ELastic Modulus / TEMPERATURE
For increasing C.L. Level (CHARLESBY)

FIG 2

Fig 3

DEFORMATION under Constant Load 125 N/cm^2





a dimensional stability of the insulation is needed even after a short circuit when the wire reaches temperature in the range of 150 or as high as 200°C for a short time.

Another particular property of CLPE concerns the ability of crystallisation. It is well known that the more irregular the PE chains are the lower the density of the material . In CLPE each cross-linking remains out of the crystallite.

So, if the cross-linking occurs in the melting state this randomly disordered chain irregularities will reduce the thickness and number of crystallites at low temperature As a consequence density modulus, hardness are reduced, flexibility, impact resistance permeability are increased.

For example cross-linking a HDPE having a density of 0,955 to 20°C, after cross-linking we obtain a product of 0,930 by quenching, an annealing would raise the density in the range of 0,940 maximum.

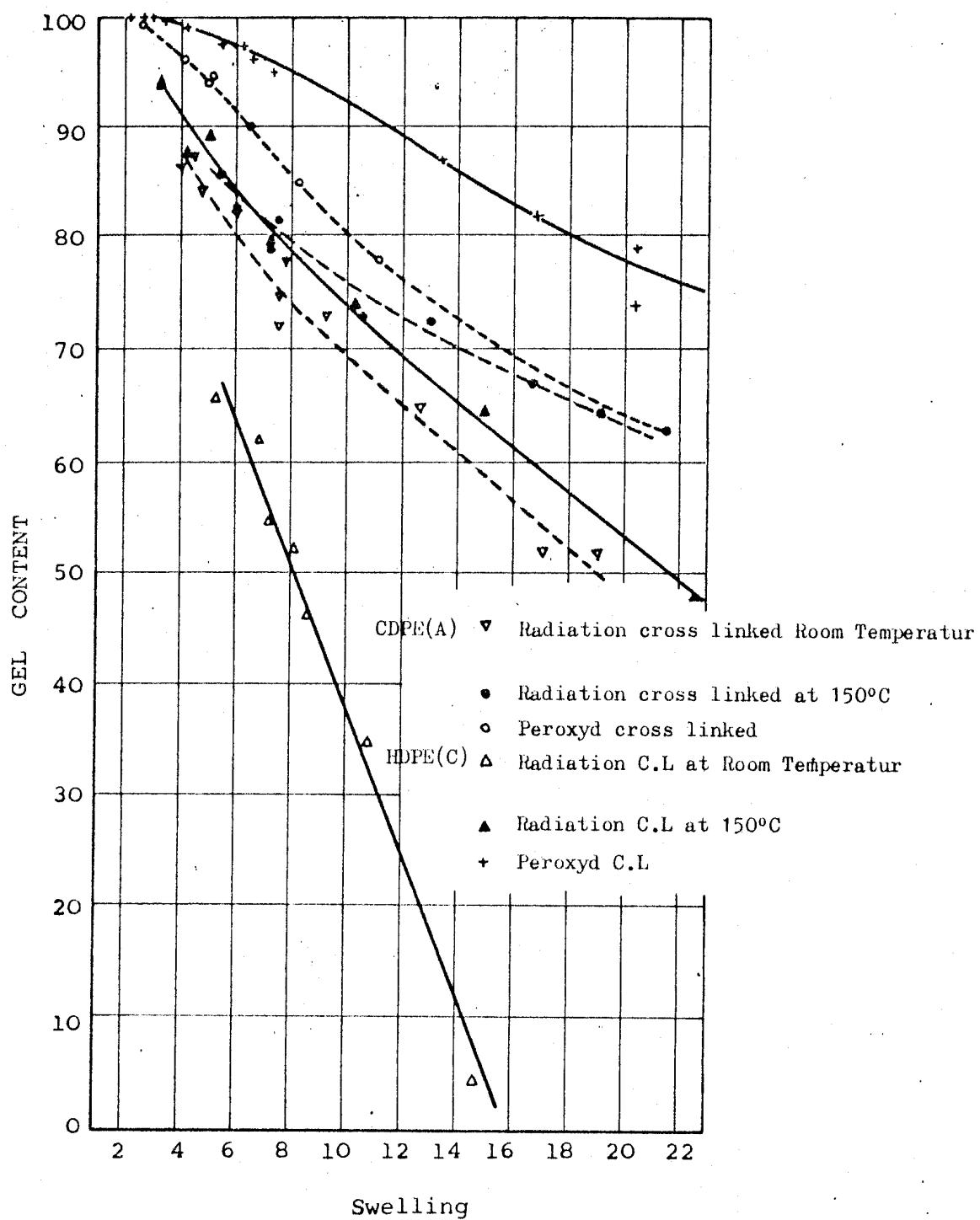
The graft CLPE are surprisingly very little reduced in density compared to raw material, since for cross-linking they need always an annealing in hot water or even in steam. However these products heated at a temperature above the melting point would crystallise on a somewhat lower density after cooling down. This is due to the fact that for these products too, the cross-linking points hinder crystalline growing.

The same behaviour is observed for β or γ ray irradiated cross-linked PE. The density difference that could exist between the original CLPE and the remelted is so much the higher that the cross-linking level and raw material density are higher.

This particularity is of great importance specially for pipes, if in order to curve easily the pipe by heating, the melting point is exceeded.

Usually the creep modulus decay for remelted β ray or silane CLHDPE is approximately 15 to 20 %.

A question which led to many controversies concerns the physical



After Dr E. Köhnlein (BASF)

Fig 5

properties difference between the hot cross-linked (peroxyde) and cold cross-linked (β , γ , silane) PE.

It is a fact that for a given gelcontent the thermomechanical properties of these two kind of polymers are different and specially their swelling ability and insolubility in solvents, the most commonly used standard characteristic of CLPE. Hermann Uwe Voigt impute this shift to the polyfonctionality of silicone linkings (more than two chains are linked together at each C.L.Point).

In fact Köhnlein has found the same discrepancy between a peroxyde and β CLHDPE and impute the shift to the distribution heterogeneity of the CL points that one can obtain in this two processes.

As an example by peroxyde cross-linking a gelcontent of 60 % corresponds to a swelling ratio of 40 % and by a irradiated sample a gelcontent of 4 % corresponds to swelling of only 14 %.

Indeed β , γ , silane cross-linking points are located in the amorphous phasis of the raw material existing before cross-linking, and are not randomly distributed along the chains, so according to the physicochemical properties examined the results are quite different. I have the feeling that from a structural point of view, there would exist a certain analogy with the thermoplastic block copolymer elastomers and conventional rubbers and these two kinds of CLPE. Clusters of tight network coexist bounded onto the lamella of cristallites.

On the figur one can see that for a same physical property, can exist a difference of roughly 10 % gel content. The only question essential for use is following . Is it possible to obtain the required specification by one or the other process and what are their limitation in reliability and costs ?

Now to conclude this chapter I would add that whatever process is used, a CLPE is only useful if the material obtained conserves his original properties a long as the product pipe, wire and others is used.

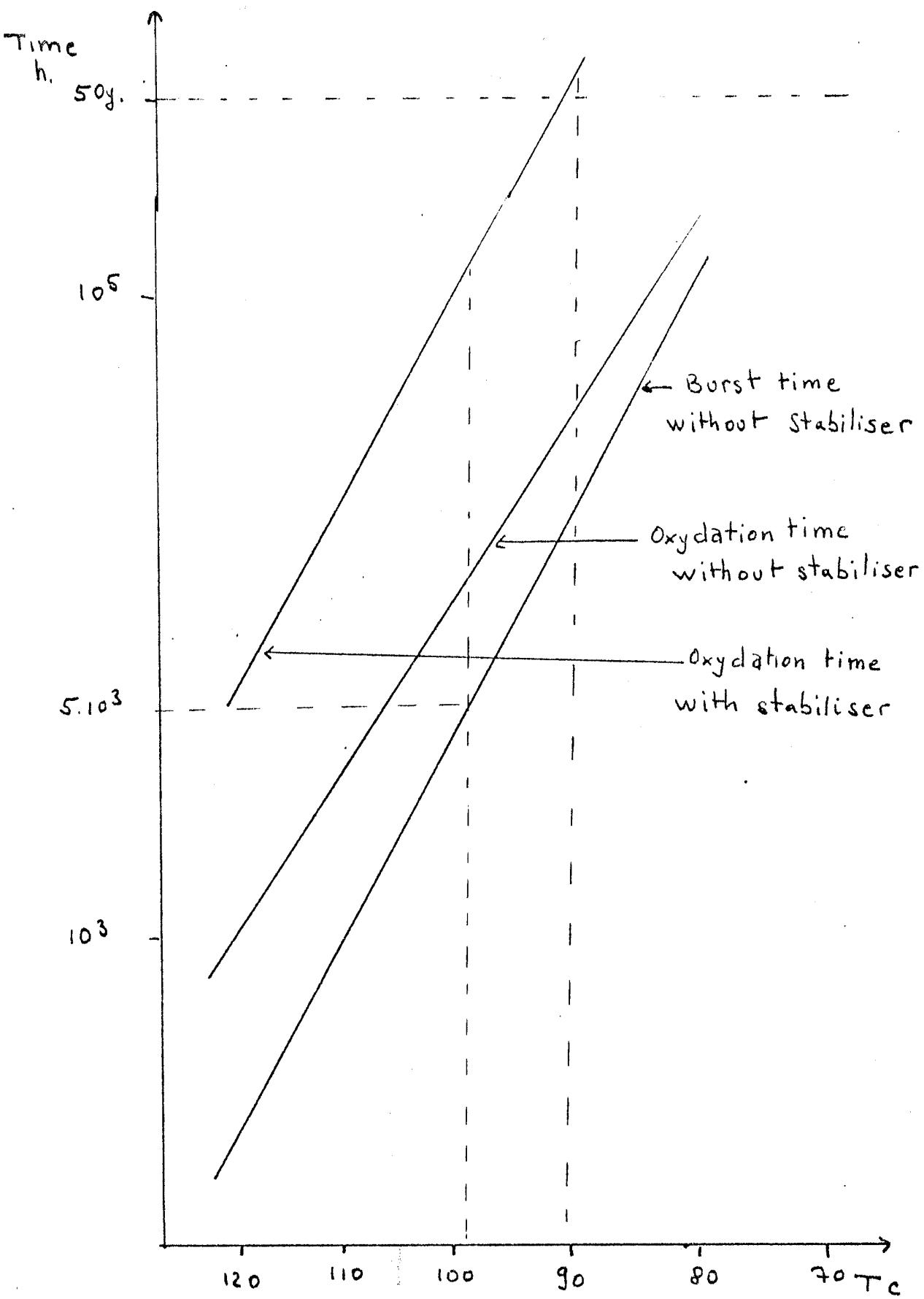


FIG 6

As the utility of cross-linking appears only on long time service or at higher temperature, this needs efficient thermooxydation stability.

If such protection is not possible or only on a quite ineffective level, the product can only be used at low temperatures, 40°C or for short periods at 90°C.

The curve here shows the oxydation time for CLPE without and with protection and one can see that without protection it is not possible to use CLPE at 90°C over 15 000 h from a simple chemical point of view. Roseen found a burst time quite independant from hoop stress of 10 000 h at 100°C on CLPE pipes not stabilised.

Very interesting is also the momory effect obtained with CLPE. The mechanism is the same as for a stretched rubber frozen in liquid nitrogen. The material cannot spring back at low temperature, here at room temperature, the orientation remains blocked by the cristallites.

At room temperature some CLPE can be streched over 500 % and they will spring back very strongly as soon as the melting point is reached. This property is used very successfully with the Raychem shrinkable sleeves and fittings for the electroengeneering industry.

Here one must notice that it is very different to cross-link first and then stretch or stretch and then cross-link. In the second case, if the cross-linking level is high there remains no more possibility for the material to spring back since all the chain orientations are blocked together by the cross-linking points, even if the raw material has been stretched over 500 to 900 %.

This phenomenon is used in pipe extrusion and also for some skin pack films irradiated after blowing. At very low dosis the mechanical properties of the film are much more increased than the shrinkability is reduced. This is due to the fact the molecular weight of PE increases very rapidly even at low irradiation dosis and as long as no network exists the shrinkability remains.

On the contrary for pipe industry, a high cross-linking level is required which can block all the memory effects.

FIG 7

INFLUENCE DE LA DOSE
D'IRRADIATION SUR
L'INDICE DE FLUIDITE

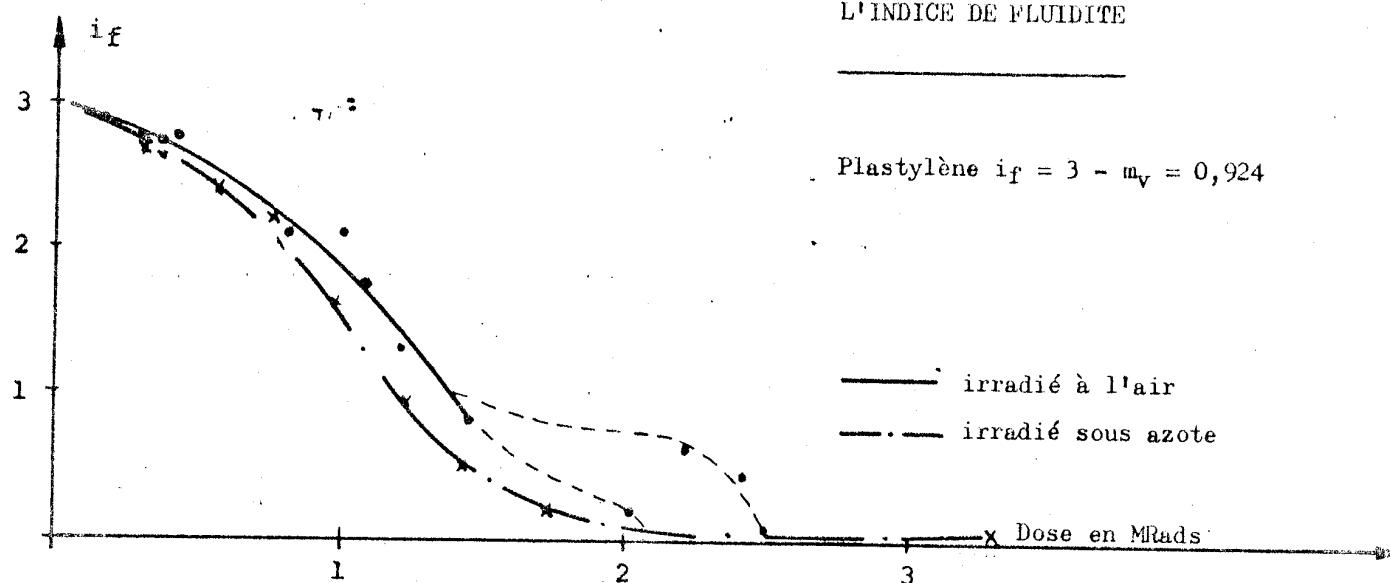
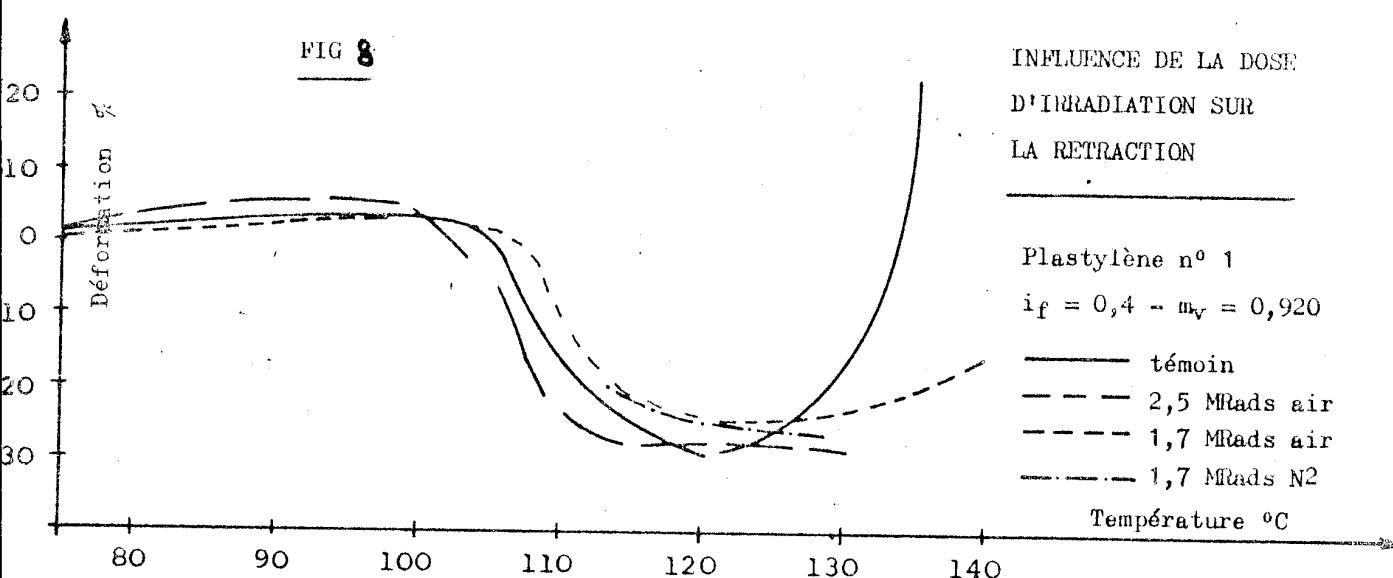


FIG 8

INFLUENCE DE LA DOSE
D'IRRADIATION SUR
LA RETRACTION



IV - We shall now describe very rapidly some typical applications and installations used for CLPE productions.

1) Films and sleeves by irradiation process: Today exists a wide range in radiation processing equipments. For CLPE three main societies use this process today in Europe on a very large scale. Two use the β irradiation. In France only Conservatome uses γ ray with a 2 M curie facility. Grace and Raychem use electron accelerators. The irradiation with the scanner are located in a blockhouse with very thick concrete walls and sophisticated safety dispositives to protect the staff; also an efficient ventilation is needed to remove the high quantity ozone generated.

To produce shrinkable films the process consists in an extrusion of a film without or only with a few stretching, to irradiate it and after that to heat the film at a temperature where blowing and stretching is practicable.

Films to be irradiated are not very thick and only low energy radiation is needed; in the range of 0,5 to 1 MEV. The dosis does not exceed some megarads and very high productivity can be achieved.

In this application Grace with his 80 accelerators has the world record as far as the number of irradiations is concerned.

In an other application Raychem irradiate and then stretch sleeves and fittings, produce pieces with much more thicker walls and needs β rays having higher energy. In fact Raychem has the world record as far as the total irradiation power is concerned. They can produce sleeves up to a diameter of 300 mm.

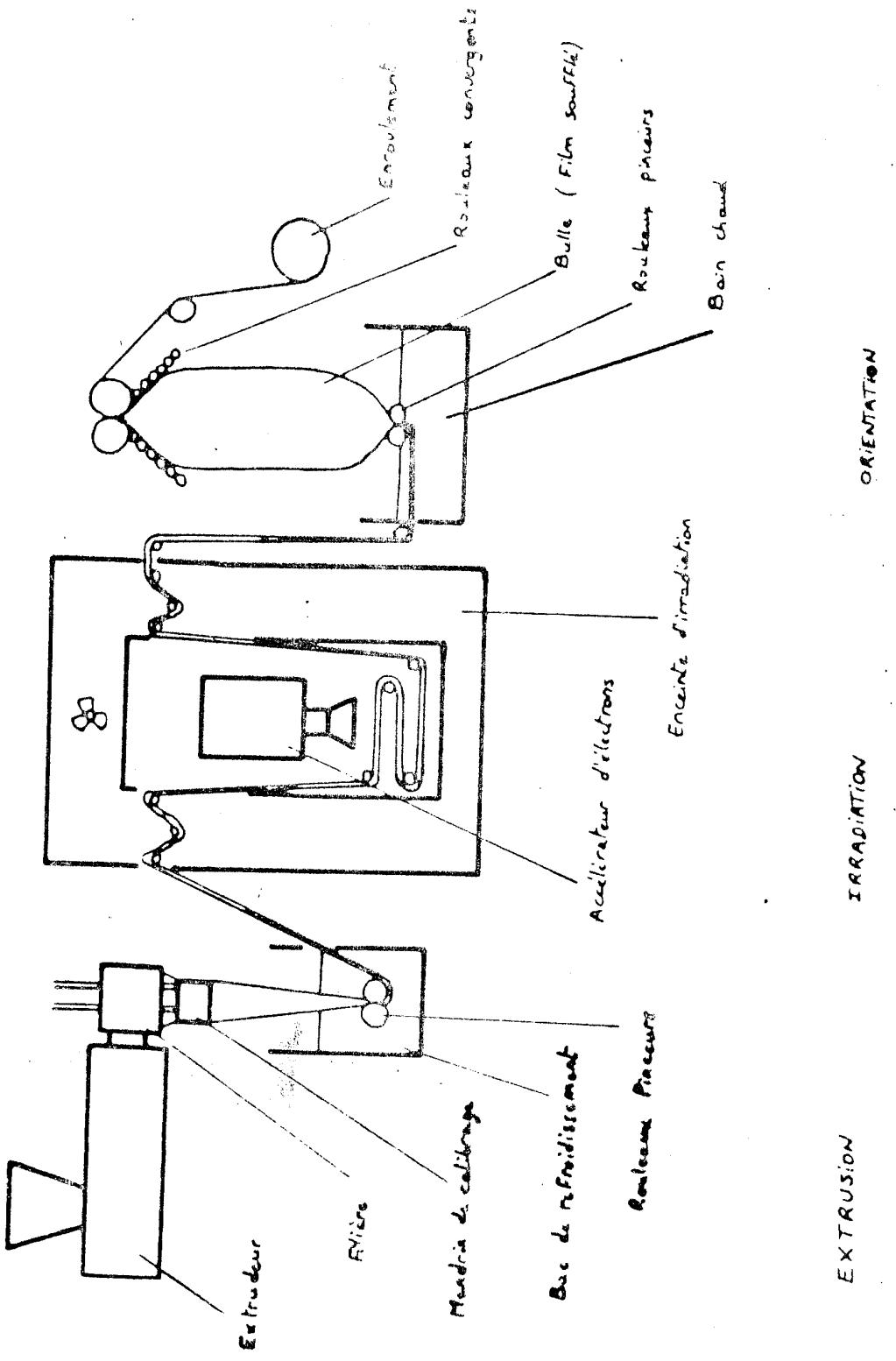
Generally speaking the high investment costs command a high utilisation level or/and good profits.

For example an irradiation of 3 MV and 50 mA costs approx. :

1,5 M \$ the irradiation
0,4 M \$ the blockhouse with accessories
0,7 M \$ the mechanical devices as Spooler and so on

Such an irradiation unit have a production of 1 000 to 4 000 t/year of irradiated products.

**PROCEDE CRYIQUE D'ORIENTATION BIAXIALE
DU POLYETHYLENE IRRADIÉ**



In another activity wire coating has been moving from paper and thermoplastic insulation to CLPE for cables of 1 KV but also progressively to 25 KV cables at the last 10 years. For higher voltage many problems must be solved but still some km of 125 KV cable CLPE insulated are testes presently.

The different processes used in wire insulation industry are base on peroxyde cross-linking or the silane cross-linking for 1 KV cable even irradiation cross-linking is used in the U. States and in Japan. In peroxyde cross-linking different processes are aviable where the cross-linking occurs in high pressure steam or in nitrogen the cable being heated with IR radiation. But other processes are in development which doesnt need so large and high buildings.

First the cross-linking in high pressure steam (18 kg) horizontal, slant, catenary and vertical lines are used.

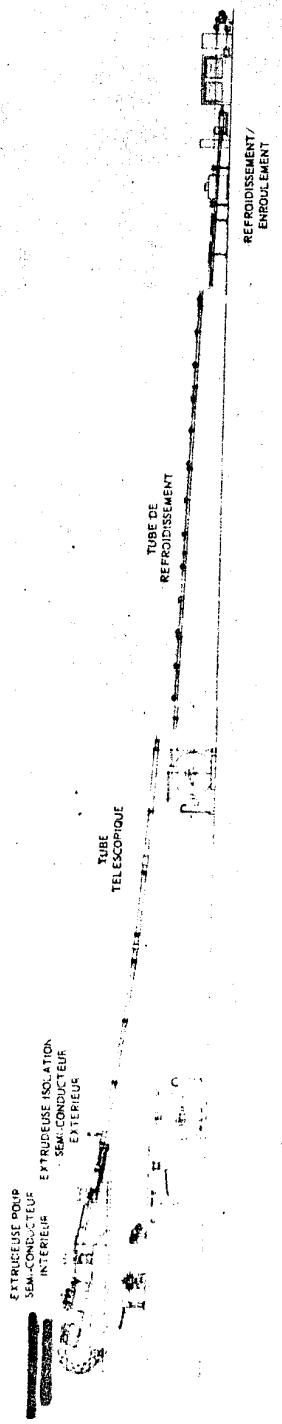
Figure 10 describes such an installation.

Pay off device - two extruders in the covering zone, then the curing zone and the same length the cooling zone. A caterpillar pull out the cable and the take up.

The output of such a line 100 m length is about 60 m/min for a cable with an insulation thickness of 1,4 mm and a total diameter of 8,4 mm (1 KV).

The output speed is reduced to 6 m/min for a total diameter of 24 mm and a insulation thickness of 6 mm (20 KV).

The most severe limitation of this process is that it is quite impossible to produce an insulation without voids. In fact at about 200°C and 18 bars a lot of water is soluble in the PE which generated microvoids of a diameter of some microns as soon as the wire has left the pressure pipe. This phenomenon limits this technique to cable for 1 KV to 20 KV.



13 18

FIG 10

To overcome this limitation and specially for cable having up to $1\ 000\ mm^2$ section a gas (Nitrogen) is used to maintain the PE under pressure, this is the Sumitomo process . The insulation is heated with irradiations up to $300^\circ C$ at the surface. The speed of the line is low enough to allow the heat transfer to the conductor.

Naturally such lines suited for high voltage insulation (up to 20 mmCPE are possible) has low output speed -about 0,4 m/min., but the cross-linked material is practically free of voids.

Today only a few km of high voltage cables are produced in this manner and this market is still in its beginning.

The third way to make CPE insulated cable is the Siplas process. Here also two possibilities exist. One, the original Dow Corning process, consist on the modification of the PE by grafting the trimethoxy-vinylsilane in an extruder and then to mix these pellets with a masterbatch of an organo-tin catalyst. The extrusion of the reactive mixture is not different as for a common PE.

Cross-linking is obtained by immersion of the cable in hot water or in a curing oven in a steam atmosphere at normal pressure.

The total water concentration in the cross-linked is the tenth of the quantity diffused in PE cross-linked at high vapor pressure.

Maillefer has developed an original process in one step in which grafting, compounding with the hydrolisis catalyst and wire coating is effected in only one operation. Of course the more different reactions must occur in precise temperature and time conditions the more precisely the process has to be conducted.

The slide shows the principe of this process and the next the extruder with the monomer, catalyst pumping devices that injects the reactives in the extruder.

However in this process too, it is difficult to cross-link very thick insulation because the diffusion time increase with the square of the PE thickness and 2 mm insulations requires a curing time of several hours. The process is suitable for cable in the range 1 KV to

perhaps 25 KV but surely not for 2 cm thick insulations.

Last no least the irradiation cross-linking is only used for small insulation thickness, since as soon the PE thickness exceed 0,5 mm it becomes very difficult to obtain a homogeneous cross-linking even if the wire rotate in the beam. Moreover one must remember that β irradiation generates round 70 ml hydrogene per Mrd/kg. As more than 15 Mrd are needed for the cross-linking a lot of hydrogene is generated in the core of the material and hasn't time to escape by diffusion and consequently generates voids.

But the process can be very useful for small cables cross-linking as for phone cables.

For example wire of 0,7 mm diameter with a insulation thickness of 0,15 mm can be cross-linked at more than 2 000 m/min. For a 27 mm wire with an insulation of 2 mm the speed is reduced to 60 m/min CLPE Insulated cables.

Pipes of CPE

These pipes designed for hot water distribution in sanitary or floor heating are produced today in Europe by the Dow Corning process and by peroxyde cross-linking. In USA one compagny produces cross-linked irrigation pipes in PE by irradiation (1 000 t year). Research and development are also running in Europe but many problems on quality, aging behaviour are not yet resolved with irradiation techniques.

Peroxyde process

The first process used in Europe to produce CPE pipes was the Engel process. This process is presently still the most used. It consists on a sintering at high pressure of the mixture of PE and a peroxyde such as ditertiobutylperoxyde for example.

The extruder is a mechanical press. A Ram forces the powdered PE at very high pressure (about 4 000 bars) trough a strainer at approximatly 140°C.

Then the material in solid states, near the melting point, is pushed in a die around the spider. Cross-linking occurs in the machine as the PE enter in the die.

Die and plunger are coated with a fluorinized coating in order to reduce shearing forces which would destroy the early network edification.

The relatively short die is heated enough to allow the extrusion of a fully cross-linked material.

The output ratio of these machines is about 20 kg/h.

Such machines are very simple and cheap. Their main disadvantage is a low productivity and the necessity to repaint the die coating at least every day.

On the other hand the mechanical necessity of a short die reduces all possibility of formulation which would delay the cross-linking.

These drawbacks became extreme for pipes of large diameter as 50 or more. Pont-a-Mousson has developed his own process of cross-linking. The process is also a sintering of powder in a cylindrical mandrel with a plunger.

The extruder is vertical and only melting occurs in the machine. The crosslinkable and molten material is then pulled through a salt bath where simultaneously, it is stretched and crosslinked.

Diameter of the pipe is adjusted only by increasing or decreasing the pulling speed which can be three or four times as fast as the extrusion speed.

The orientation of the material which would cause a springback of the PE cannot work after cross-linking since the chains are blocked segmentally the one to the other. (Even a ten times stretched and cross-linked material has no memory effect).

The machine has a output of 30 kg/h and works 24 h a day, 5 days a

Extrudeuse verticale à piston annulaire et bain de sel

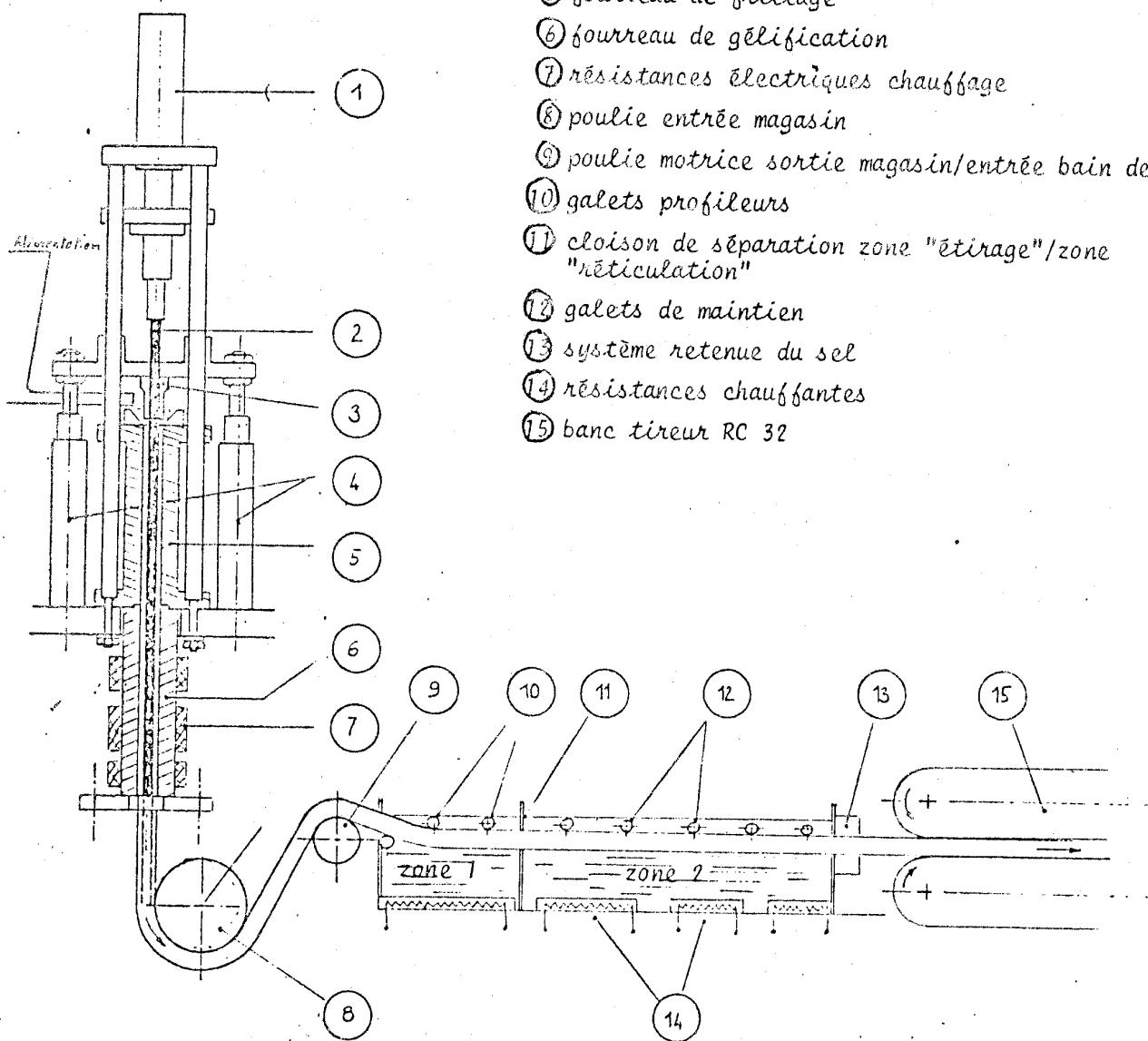


FIG 11

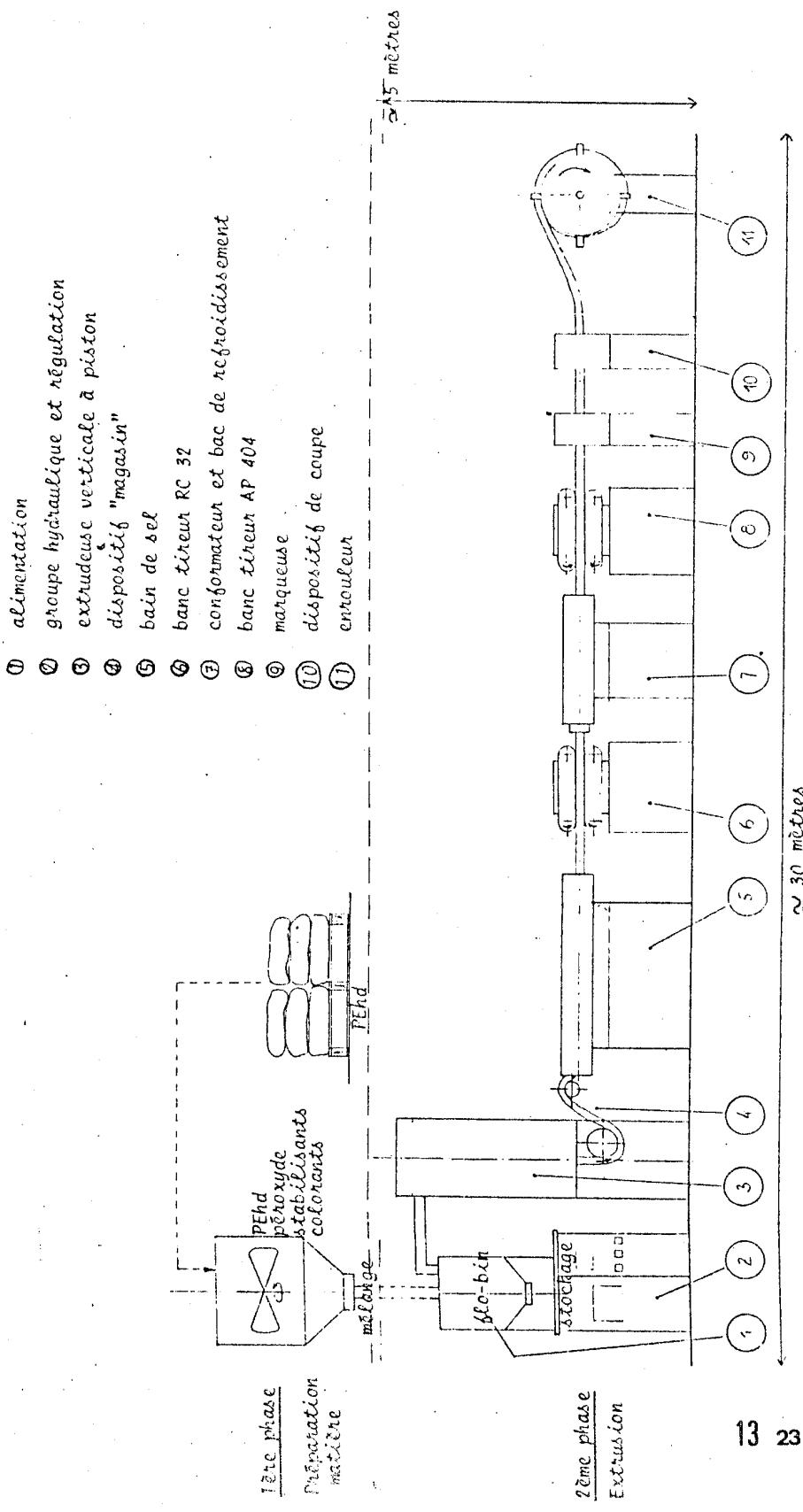


FIG 12

week automatically and no tool cleaning is necessary.

The main advantage of this process is the possibility to regulate separately the extruder and the cross-linking unit.

An other and very important advantage is that in the salt bath there is time enough to adjust very precisely cross-linking speed and final level. So it is possible to introduce the stabilizers with the needed effectiveness for a long term protection against oxydation - in smooth cross-linking conditions.

A third producer Lubonyl in Sweden is starting with an other process consisting in an extrusion with a conventionnal twin screw extruder, of a sophisticated formulation and then in crosslinking in a salt bath as we do.

The process may have good chances in the future. It is still in development.

Sogecan in France, British Steel in England and Granges in Sweden use the Dow Corning process for CPE pipes.

Noteworthy is that here all the problems and the know how consists in the good choice a suitable PE as raw material - a good control the grafting conditions with a good designed extruder screw.

Then it is possible to extrude a pipe quite as easily as with common PE. The bobbins are cured in hot water or in an oven with a steam atmosphere at 100 to 110°C.

If immersion time is not a limitating factor this technique should permit to produce economically large cross-linked pipes.

Just now some words to mention the cross-linked PE foams patented by Funrkawa and developped in Europe by Bayer-Frelen.

The raw material is a LDPE compounded with dicumylperoxy or an other and a blowing agent master batch.

The extruded sheet is cured in an oven in very precise time and temperatur conditions in order first to foam and then cross-link. Density can be adjusted between 30 and 150 kg/m³ for foams with closed cells.

The production of such foams is approximatively round 3 000 t/year. In USA the same material is produced by irradiation. CPE foams are used in packaging, as phonnic and thermic insulation.

Now I am going to conclude with some considerations for the future of the different materials.

In the electrical application it is well established that CPE insulation will progressively replace PVC or normal PE.

Besides, there is a strong interest for higher tension insulation particularly 60 KV and over. But very important progresses must be done to achieve a sufficient reliability and productivity for CPE insulation at so high tension.

In the very next future CPE insulation will first progress in the medium tension wire market.

Many laboratories in France, Germany, Japon work on new processes with shorter and cheaper extrusion lines.

As far as pipes are concerned, floor heating would be, for some years a strongly increasing issue. But also more technical applications are studied as for example cooling tower or off shore flexible pipe linings.

Considering the processes the peroxyde ones have to increase the output of the different machines. Sioplas as well as irradiated pipes can be successful ways in future if quality can be raised to the required level.

In packaging the technical interest of strong shrinkable films and the high productivity of packaging lines will insure growth for the future to product such as the well known Cryovac films.

I thank you for your kindly attention.

SOCIETY of PLASTICS ENGINEERS

First EURETEC

Gent, June 14 - 15, 1979

THE GROWING DIVERSITY of
ETHYLENE COPOLYMERS

Rudolph D. Deanin
Professor of Plastics
University of Lowell
One University Avenue
Lowell, Mass. 01854, USA

Index
A/H

THE GROWING DIVERSITY OF ETHYLENE COPOLYMERS

Rudolph D. Deanin

Plastics Engineering Department, University of Lowell,
Lowell, Massachusetts 01854 USA

Polyethylene enjoys low-cost synthesis from petroleum, and easy thermoplastic processing to a wide range of products which benefit from its useful balance of properties. It also enjoys a simple molecular structure which forms the basis for structure-property theory in polymer science. Beyond the simple linear homopolymer, copolymerization provides us with a much broader variety of useful properties, and structure-property relationships, which we have barely begun to explore and exploit. A review of these can indicate the trends and suggest the directions for future research and development.

OLEFIN COPOLYMERS

1-Butene copolymer is the most common and best established. Addition of about 5% of 1-butene to the polymerization reaction reduces crystallinity about 10% and density about 1%, thus reducing tensile strength and melting point, but increasing ultimate elongation and creep resistance. The major improvement is environmental stress-crack resistance, which is very important for application in bottles, pipe, and wire and cable insulation.

Low-Density Polyethylene is a homopolymer to the polymerization engineer, but the chemical analyst who characterizes its structure finds it a random tetrapolymer, mainly ethylene units mixed with a few percent each of 1-butene and 1-hexene units and a very small percent of divinyl branching function. We have actually produced LDPE in a low-pressure Ziegler-type polymerization by adding a few percent each of 1-butene and 1-hexene; but literature and patent reports suggest that the same structure might be produced more economically simply by adjusting the catalyst in a low-pressure "homopolymerization" reaction. In any case, the random tetrapolymer structure fortuitously produces a moderate degree of crystallinity which is responsible for the familiar leathery flexibility and easy processability of LDPE.

Ethylene/Propylene Rubber is a random copolymer in which we intentionally prevent crystallinity in order to produce maximum rubbery softness and flexibility. Being a saturated elastomer, it has good resistance to oxygen and ozone aging, and its low price makes it additionally attractive. The difficult peroxide vulcanization has been remedied by terpolymerization with non-conjugated diene termonomer such

as dicyclopentadiene and ethylidene norbornene, which permit fairly conventional sulfur vulcanization.

Thermoplastic Elastomers based on EPR have recently become available from companies including DuPont, Goodrich, and Uniroyal. These appear to be 2-phase polymer systems in which an ethylene/propylene random copolymer forms the continuous matrix, providing soft rubbery properties; while polypropylene forms the hard micro-particles of dispersed domains which act as "thermoplastic cross-links," combining thermoplastic processability with good strength properties. It is not clear whether the polypropylene is combined by simple polyblending or by block or graft copolymerization. In any case, these thermoplastic hydrocarbon elastomers combine thermoplastic processability and rubbery properties with good resistance to oxygen and ozone aging.

A particularly intriguing member of the family is Shell Kraton G, a saturated relative of their original styrene/butadiene/styrene sandwich block copolymer thermoplastic elastomer. The new saturated version is variously reported to contain middle blocks of ethylene/propylene rubber, ethylene/butylene rubber, or hydrogenated polybutadiene. In any case, it is designed to combine thermoplastic processability, rubbery properties, and resistance to oxygen and ozone.

Polyethylene/Butyl Rubber Graft Copolymer has been developed by Allied Chemical Corporation, with properties intermediate between the two homopolymers but superior to simple blends. These graft copolymers are thermoplastic polyolefins with modulus lower than straight polyethylene, and elasticity, impact strength, and stress-crack resistance greater than straight polyethylene. Rubbery behavior is generally slower and stiffer than straight butyl. Most likely applications are in bag liners for railroad freight cars, hose and tubing, and similar mechanical products. High carbon black loading produces volume resistivities below 100 o.c. for antistatic applications. And addition to polyethylene improves foam processing.

ETHYLENE/VINYL ACETATE COPOLYMERS

The most versatile family of ethylene copolymers is produced by random copolymerization of ethylene with vinyl acetate in the conventional high-pressure process. While molecular weight and branching are undoubtedly important, the primary variable is the vinyl acetate content, which may cover the entire range from 0 to 100%, producing a broad spectrum of properties and applications at low cost.

Modified Polyethylene contains about 9-10% vinyl acetate, and produces films which are softer, clearer,

and glossier, for cling wrap and stretch film packaging.

Soft Flexible Copolymers containing 19-45% vinyl acetate resemble plasticized polyvinyl chloride, except that they are permanently plasticized. Moldings and extrusions have low modulus, high stress-crack resistance, and good low-temperature flexibility. When used for wire and cable insulation, they are superior to polyethylene in extrusion rate, cross-linking, and flexibility.

Elastomers are generally copolymers containing 45-60% of vinyl acetate and vulcanized with peroxide. Being saturated and polar, they offer oxygen- and oil-resistance at low cost. Their excellent age resistance makes them a prime candidate as encapsulant for photovoltaic solar energy cell construction.

Wax Fortification is provided by copolymers containing 18-33% vinyl acetate. When added to hot-melt wax coatings, these copolymers provide increased flexibility, strength, gloss, clarity, and barrier properties.

Adhesives are formulated from copolymers containing 18-60% vinyl acetate. These may be applied from hot melt or solution, and used as hot melt, heat-seal, solvent, or pressure-sensitive adhesives, thus providing a great versatility in application as well as in the range of polarity and compatibility for formulation and application to various substrates.

Polyvinyl Chloride benefits from compounding with EVA copolymers. Copolymers containing 30-45% vinyl acetate are weather-resistant impact modifiers for rigid vinyls. Copolymers containing 55-60% of vinyl acetate are permanent polymeric plasticizers for flexible vinyls. Both types of application enter a large competitive field, and may offer distinct advantages over earlier materials.

Latex of high vinyl acetate/ethylene ratio has been field tested in applications such as latex paint, but the commercial possibilities remain to be clarified.

Ethylene/Vinyl Alcohol 25/75 copolymer is made by hydrolysis of EVA, producing an engineering thermoplastic which melts at 186°C and is strong, creep-resistant, antistatic, track-resistant, and solvent-resistant. This has been offered commercially in both unreinforced and glass-fiber-reinforced grades.

ETHYLENE/ACRYLIC ESTER COPOLYMERS

Acrylic esters resemble vinyl acetate in their ability to break up the regular crystalline structure

of polyethylene, making it more soft, flexible, and particularly rubbery. As saturated age-resistant elastomers, they appear superior to ethylene/vinyl acetate.

Methyl Acrylate Copolymer is available as a heat- and chemically-resistant elastomer of moderate price. It contains a few carboxylic acid groups for cure by diamines such as methylene dianiline. It is superior other oil- and weather-resistant rubber in many ways. It is less expensive than fluoro and silicone rubbers, superior to fluoro rubber at low temperature, and superior to silicone in strength. Heat resistance to 150°C is superior to chlorosulfonated polyethylene and nitrile rubber. Main use is in automotive parts.

Ethylene Acrylate Copolymers have competed with vinyl acetate copolymers for some time, but their superiority is primarily in heat resistance and low-temperature flexibility of the elastomers. Applications are primarily in hose, wire and cable, and toys.

ETHYLENE/ACRYLIC ACID COPOLYMERS

Copolymers containing 3.5-8% of acrylic acid are superior to straight polyethylene in strength, toughness, hot tack, and adhesion, justifying their 50% higher price for applications such as adhesive layers in extruded laminates, heat-activatable adhesives, and skin packaging.

Ionomers contain 8% of acrylic acid 50% neutralized by sodium hydroxide. This reduces crystallinity to 11%, and produces ionic clusters 100 Å diameter which act as thermoplastic cross-links. This produces an easy-processing thermoplastic with high melt strength, giving moldings and films which are stiff, strong, tough, adhesive, clear, oil-resistant, and stress-crack-resistant. Major uses are as adhesive layer in laminates, heat-seal layer in food-packaging film, golf ball covers, auto bumper pads and rub strips, and shoe parts such as soles, heels, toes, and counters.

CHLORINATED POLYETHYLENES

Instead of chlorinating ethylene and then polymerizing to polyvinyl chloride, it is perfectly possible to polymerize ethylene and then chlorinate it to a great variety of structures with a much greater variety of properties. The main independent variables are the type of polyethylene and the chlorination conditions. Commercial development has concentrated on random chlorination of high-density polyethylene, inserting 25-48% of chlorine to break up the regularity and crystallinity and produce soft rubbery polymers. These have found a number of promising

applications:

Vulcanized Elastomers are made by peroxide or radiation cross-linking. These are superior to EPDM, chlorosulfonated polyethylene, chloroprene, and nitrile rubber in heat, flame, oxygen, ozone, oil, chemical, and weather resistance, and are reasonably low in cost. Chlorine content of 25-36% is used for wire and cable insulation; 36% is considered general-purpose rubber, good for plasticizer compatibility, low set, and low-temperature flexibility; 42% is preferred for hardness, tear strength, flame resistance, oil resistance, and impermeability. Major uses are in hose, tubing, and mechanical goods of various types.

Polyvinyl Chloride Compounding is another promising area for chlorinated polyethylenes. As impact modifiers in rigid vinyl, they give high impact strength and resist outdoor aging. As permanent plasticizers in flexible vinyl, they show particular promise in flooring.

Polyblending appears to be an area of general promise. By adjusting the chlorine content and distribution, it is possible to produce compatibility with a wide variety of other polymers, and perhaps even use CPE as a compatibilizer. Addition to polyethylene and to elastomers contributes the flame retardance of the chlorine content.

Ethylene/Vinyl Chloride Copolymers offer an alternative way of producing such a range of chlorine contents. These have been studied in research and development, but still await successful commercial application.

FLUOROPOLYMERS

Recently ethylene has been introduced as a comonomer in fluoropolymers to provide internal plasticization for easier processing. The primary objective has been heat-resistant wire and cable insulation.

Ethylene/Tetrafluoroethylene 25/75 copolymer can be extruded readily onto wire and cable for aircraft and computer wiring. It is stronger and tougher and more elastic than straight PTFE or FEP.

Ethylene/Chlorotrifluoroethylene 20/80 copolymer is fairly similar, but designed for chemical process equipment, especially chemically-resistant linings for such equipment.

PROSPECTS

This broad variety of commercial ethylene

copolymers has developed in the past 20 years, and is growing rapidly in volume, variety, and utility in many directions. It indicates immediately many areas for aggressive practical technical and commercial development.

Further in the future, there are a greater variety of copolymerizations remaining to be explored. Some of these have appeared only in basic research, others not at all. All of the vinyl monomer and polymer systems may be considered as immediate candidates for modification by copolymerization with ethylene; and graft and block copolymerization opens the field to all other types of polymers as well. More difficult but also more challenging are dissimilar addition reactions such as hydrogen addition and oxidative polymerization, ring opening, isocyanate reactions, and so on. Considering the availability and economics of ethylene and the proven utility of so many of its copolymers, many of these deserve the energetic scrutiny of enterprising organic polymer chemists and product development engineers.

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Gent, June 14 - 15, 1979

D. Rabek

A. Rabek

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UV DEGRADATION of

POLYOLEFINS

Jan F. Rabek and

Bengt Ranby

Department of Polymer Technology

The Royal Institute of Technology

Stockholm, Sweden

UV DEGRADATION OF POLYOLEFINS.

Jan F. Rabek and Bengt Ranby, Department of Polymer Technology,

The Royal Institute of Technology, Stockholm, Sweden.

Polymers currently used on a large scale may be divided into three groups depending upon their resistance to photodegradation:

1. Highly photostable polymers which are used without photostabilizers added, e.g. poly(tetrafluoroethylene) and poly(methyl methacrylate).
2. Moderately photostable polymers which can be used without photostabilizers, e.g. poly(ethylene terephthalate) and polycarbonates.
3. Poorly photostable polymers which need extensive stabilization for outdoor uses, e.g. polyolefins, poly(vinyl chloride), polystyrene, nylons, rubbers and cellulose.

The definition of long-term photostability of polymers and polymeric materials differs depending on their application. For the packaging industry 1-4 years are required, whereas for the building and machine industries, 10-40 years. All of these industries are interested in the photosensitized reactions which accelerate polymer oxidation and degradation.

Considering the structure of common polymers they contain mostly C-C, C-H, C-O, C-N and C-Cl bonds and should not absorb light of longer wavelength than 190nm, i.e. they should not be photodegradable by sunlight.

UV-spectroscopy measurements show that most commercial polymers have increased absorption at wavelengths > 190 nm which is due to internal and external impurities.

The external impurities may originate from:

1. Manufacture of monomers
2. Polymerization process, e.g. initiator residues
3. Processing and storage of products.

The internal impurities are due to the formation of different chromophoric groups or to the initiator residues attached to the polymer chains.

Industrial polymers are contaminated during recovery, processing, and storage. In most cases the history of a polymer is incompletely known. The protection of an industrial process may not allow information, e.g. about the composition of catalysts added, parameters of polymerization and recovery processes, etc. It can therefore be difficult to specify what kind of impurities may be present in commercial products offered and to predict what kind of accelerated photo-reactions may occur.

In order to characterize a typical photo-sensitized reaction the following data are required:

1. The excitation process and the nature of the excited state of the compound from which the energy is transferred.
2. The nature of the energy transfer process, i.e. quantum efficiency, rate constant, temperature dependence, etc.
3. The nature of the excited state of the reacting polymer molecule which is sensitized and the resulting reaction or molecular rearrangement.

In practice photo-sensitized reactions are classified according to the chemical nature of the sensitizer ('impurities) or the presence of chromophoric groups. All photochemical reactions occur as a result of electronically excited states which have definite energy, structure and lifetime, and are involved in the photo-induced processes. The most important states are: singlet excited states - states with paired electron spins; triplet excited states - states with two unpaired electron spins (possess a net spin magnetic moment of 1). The excitation energy of a molecule in its excited state may be dissipated by:

1. Radiative processes (fluorescence and/or phosphorescence)
2. Radiationless processes (heat)
3. Energy transfer processes

4. Dissociation processes (with formation of free radicals).

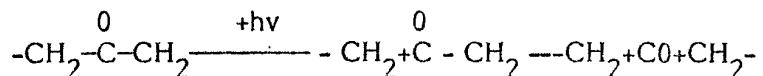
Polyolefin photochemistry (photodegradation, photooxidation and photostabilization) has been discussed in a number of papers, reviews and textbooks¹⁻⁵. The commercial polyolefins are low and high density polyethylenes, polypropylene and poly(4-methyl-1-pentene).

The major technical photochemical problems are concerned with the sensitized degradation of polyethylenes and their stabilization.

The main light-absorbing impurities (internal and external) which act as sensitizers are groups attached to the polymer chains, e.g. hydroperoxides⁶⁻¹¹, dienes⁸, trienes¹² and oxygen-polymer charge transfer complexes¹³⁻¹⁶, aromatic compounds¹⁷⁻²⁰, and metallic impurities²¹⁻²⁴. The commercial polyolefins irradiated with UV exhibit both fluorescence and phosphorescence (radiative processes)^{4, 17-20, 25-34} from impurities present, that may initiate photodegradation processes in the polymer^{1-5, 33, 35-38}.

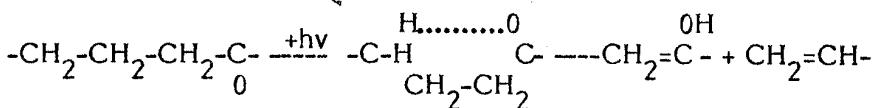
The initiation and propagation mechanism, for photodegradation and photo-oxidation of polyolefins depends mainly on the presence of different types of impurities. Two primary photochemical processes are believed to be responsible for the carbonyl-initiated photodegradation of polyolefins:

1. Norrish type I process, which leads to the formation of free radicals:



The excited singlet or triplet states of the carbonyl groups are precursors to the reactions.

2. Norrish type II process, which only occurs when the ketone possesses at least one hydrogen atom on the α -carbon with respect to the carbonyl group. The reaction occurs via a six-membered cyclic intermediate involving intramolecular hydrogen-atom abstraction. It produces one olefinic and one enolic group in the polymer:



Studies of the luminescence from commercial polyolefins have made a significant contribution in understanding of the mechanism involved in photoinitiation by carbonyl groups^{4, 17-20, 25-38}.

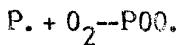
The initiation process of photodegradation process may also occur by formation and photodecomposition of hydroperoxides^{1-8, 10, 11}.

Alkyl peroxides have absorption spectra extended from far ultraviolet to 330 nm (near ultraviolet). These groups are capable of absorbing sunlight of wavelengths which are photochemically harmful to the polyolefins. Hydroperoxide groups are formed according to the following mechanism:

1. Formation of polymer alkyl radicals (P_\cdot) by abstraction of hydrogen from polyolefins, e.g. by a free radical formed from light-excited impurities (R_\cdot):

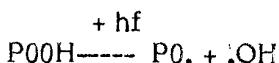


2. Polymer alkyl radicals (P_\cdot) can easily react with molecular oxygen, producing peroxy polymer radicals (POO_\cdot) by addition:



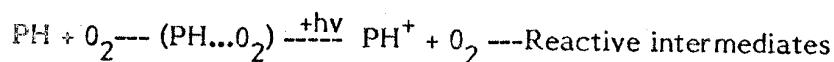
3. Polymer peroxyradicals ($\text{P}00.$) may abstract hydrogen from the same or from a neighbouring polymer molecule (PH):
 $\text{P}00.\cdot + \text{PH} \rightarrow \text{POOH} + \text{P}.$

4. Hydroperoxy groups can easily be photodecomposed by UV-light:



Electron spin resonance (ESR) spectroscopy has provided valuable information on the nature of radicals formed (R_\cdot , $\text{R}00_\cdot$, and $\text{R}0.$) produced during photodegradation and photooxidation of polyolefins^{2,3}. It is generally accepted that hydroperoxides formed during processing are the main photoinitiators in commercial polyolefins and may be precursors to carbonyl group formation.

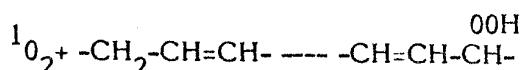
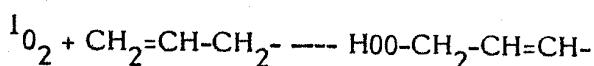
Polyolefins saturated with oxygen exhibit an increased absorption which is attributed to oxygen-hydrocarbon charge-transfer (CT) complexes¹³⁻¹⁶. The excited CT complexes are believed to initiate photooxidation of polyolefins by the following mechanism:



Research during the last decade has demonstrated the role of singlet oxygen (${}^1\text{O}_2$) in photooxidation of polymers³⁹⁻⁴³. Singlet oxygen (${}^1\text{O}_2$) is an excited form of molecular oxygen (${}^3\text{O}_2$) which in the ground state exists as a triplet state. Singlet oxygen exists in two excited states:

	Excess energy	Lifetime in gas phase (low pressure)	Lifetime in solution
${}^1\text{O}_2({}^1\text{g})$	22.6 kcal	45 min	H_2O (2 u s) - CCl_4 (700 u s)
${}^1\text{O}_2({}^1\text{g}^+)$	37.6 kcal	7 sec	-

Singlet oxygen reacts with polyolefins by the ene mechanism^{6,43}:

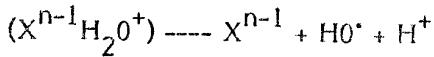
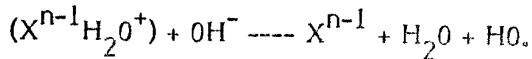
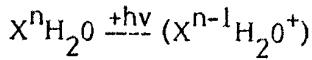
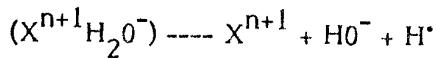
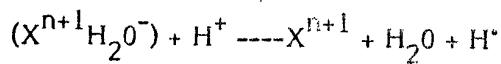
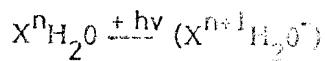


Singlet oxygen in polyolefins can be formed in the following ways:

1. In photosensitizing reactions due to traces of impurities present, e.g. polynuclear aromatic hydrocarbons, e.g. anthracene, napthalene, pyrene, benzo(a)pyrene, 1,2,3,4-dibenzanthracene and chrysene which may efficiently generate singlet oxygen. The presence of polynuclear hydrocarbons in the atmosphere is a result of increasing industrial and urban development. The growing consumption of fossil fuels by burning produces several different air pollutants⁴⁴. Polyolefins have a tendency to absorb on the surface polynuclear aromatic hydrocarbons released into the atmosphere from combustion processes^{20, 45, 46}.
2. In energy transfer reactions between the excited triplet state of chromophoric groups (e.g. carbonyl groups) in a polymer backbone chain and molecular oxygen.
3. Surface reactions of polyolefins by singlet oxygen (and also by atomic oxygen and ozone) which is formed in photochemical reactions occurring in polluted atmosphere of water in the environment of the polymer sample.

Singlet oxygen may play a considerable role at the beginning of a degradation process, because its reaction with polyolefins increases the concentration of hydroperoxide groups. Subsequent chain scission may occur by a free radical mechanism, without further participation of singlet oxygen. Free radical oxidation processes occur simultaneously and cannot be avoided or excluded due to the presence of molecular oxygen. Some kinds of free radicals are formed from the photosensitized decomposition of hydroperoxide groups, while others may be formed from direct photolysis of impurities, additives, etc. For that reason it is difficult to determine the true role of singlet oxygen in the photooxidation of polyolefins.

It has been shown that certain metallic impurities, particularly Ti and Fe, can efficiently sensitize the photooxidation of polyolefins²¹⁻²⁴. Polyolefins obtained by polymerization in the presence of Ziegler-Natta-type catalysts always contain transition-metal residues, e.g. of titanium (50 p.p.m.) which cannot be easily removed. These metallic impurities absorb near UV radiation and by electron transfer from one ion to another or to a polymer molecule they may produce free radicals:



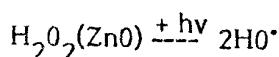
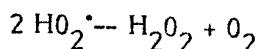
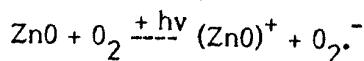
The presence of water plays a considerable role in these reactions.

The ash residue from Ziegler-Natta catalysts ($TiO_2 - Al_2O_3$) may cause photochemical crosslinking of polypropylene²⁴.

It should always be considered that polyolefins manufacturers on an industrial scale contain various metallic impurities such as metal oxides and salts or residues of metal organic catalysts from various sources:

1. Chemical and atmospheric corrosion of apparatus used in chemical processes.
2. Processing machinery, e.g. rollers, calenders and extruders.
3. Packaging materials.

In order to colour polyolefins for commercial use, inorganic pigments are added, like metal oxides. Several pigments have the ability to protect the polymer by a screening effect. White pigments like ZnO or TiO_2 show high ultraviolet reflectance within the 300-400 nm range. On the other hand inorganic pigments markedly photosensitize the degradation of polyolefins. The photoactivity of metal oxides may be attributed to radical anion (O_2^-) formation^{32, 33, 47-51}:



The hydroxyl ($HO\cdot$) and hydroperoxy ($HO_2\cdot$) radicals may abstract hydrogen from polyolefins and thus initiate β -scission and oxidative degradation.

The degradation of polyolefins under UV light can be decreased and delayed by adding photostabilizers. In order to stabilize polyolefins against UV light it is necessary to know:

1. The content of impurities introduced during polymerization, processing, storing and finishing of polyolefins.
2. The mechanism of degradation of a particular type of polyolefins.
3. The role of structural irregularities. Branched polyethylene is for instance more easily photooxidized than linear polyethylene. Oxygen attacks only the amorphous part of a semicrystalline polymer.
4. The mechanism of photolysis of additives. All additives including light stabilizers should be examined for light stability. It should always be considered that organic compounds are photolysed by UV light in the range 220 - 400 nm into free radicals, which may initiate polymer degradation and free radical oxidation.
5. The mechanism of stabilization of a particular, absorption of radiation, quenching of excited states of chromophoric groups or impurities in the polymer, decomposition of hydroperoxides, scavenging of free radicals, etc.
6. The inability of a stabilizer to decrease and delay but not prevent degradation completely, due to different mechanisms, e.g. removal by chemical reactions, photolysis, chain initiation via oxidation of the stabilizer, chain initiation by stabilizer radicals, antagonism with other additives, effect of crosslinking, loss through volatilization, solubility or migration, staining or discolouration due to the additives, etc.

It is apparent that the degradation of commercial polyolefins is exceedingly complex, since processing and small quantities of impurities or additives can interact with stabilizers and totally change the behaviour of the substrate. It is not sufficient to examine the effects of the stabilizers on the degradation process. The pure polymer must be studied as a reference. To obtain the full story the polymer must then be studied as a reference. To obtain the full story the polymer must then be studied in the presence of known impurities (sensitizers) and stabilizers added one by one and in combination. This systematic approach to study stabilization of polyolefins is laborious and requires information on the degradation also of model compounds and pure materials.

There are several factors which are important in the choice of photostabilizer for a certain polyolefin:

1. Solubility (compatibility) of the stabilizer in the polymer phase.
2. Ease of compounding the stabilizer with the polymer.

3. Rate of stabilizer loss from the polymer phase through migration, exudation, volatilization and other processes.
4. Initial colour and colour change in the stabilized polymer due to exposure to UV light or heat.
5. Heat stability and light stability.
6. Chemical reactivity of the stabilizer with the polymer or impurities present in the polymer.
7. Toxicity of the stabilizer.
8. Cost of stabilizer and its application. Photostabilization of polyolefins can be achieved in many ways ^{2, 4, 5}:
 1. Screening of the radiation by preventing the penetration of UV radiation into the material
 2. Absorption of the radiation.
 3. Quenching processes for excited states.
 4. Peroxide decomposition into harmless compounds.

The most common stabilizers for polyolefins used commercially can be divided into four general categories:

1. Inorganic and organic pigments, as iron oxides (Fe_2O_3 and Fe_3O_4), zinc oxide (ZnO), titanium oxide (TiO_2) and carbon black. They act as screens and the light is prevented from being absorbed by the photoactive chromophoric groups or impurities in the polymer. They are also sensitizers as previously mentioned.
2. UV-absorbers, e.g. 2-hydroxybenzophenones or 2-hydroxybenzotriazoles, which absorb UV light and then dissipate the excitation energy by a mechanism involving the reversible formation of a six-membered hydrogen-bonded ring ^{2, 4, 5, 52}:

This mechanism explains the stabilization effect of 2-hydroxybenzophenones where the energy from absorbed UV is dissipated by formation of an enol form from a keto-form. The enol-form is thermodynamically unstable, and a reversible reaction to keto-form occurs within the time 10^{-9} s.

3. Excited state quenchers, e.g. transition metal acetyl acetonates and metal chelates like nickel acetophenone oxime ⁵³⁻⁶¹. Most chelates operate by quenching the excited states of chromophoric

groups, singlet oxygen (physical quenching) but they may also react as free radical scavengers. Presently, a series of Ni(II) chelates are marketed as most effective stabilizers for polypropylene.

4. Peroxide decomposers, e.g. dithiophosphates or dyclic phosphite esters⁶²⁻⁶⁵, which react as powerful Lewis acid catalysts for the decomposition of hydroperoxidized.

Lately hindered amines are discovered to be a new group of active photostabilizers for polyolefins. Users concerned about compatibility, reactivity and toxicity of these new photostabilizers have prompted extensive testing to assess the full value of this innovative approach to light stabilization.

Additives such as photostabilizers and antioxidants of low molecular weight may evaporate during the moulding and extrusion processes (polyethylene 200 - 220°C and polypropylene 210 - 270°C) and may also migrate from the products during storage. There are three ways of overcoming these problems:

1. By attacking the UV absorbers to polymer chains in a chemical or physical manner, e.g. by introducing reactive, polymerizable or solubilizing groups into the additive.
2. By preparing polymeric UV absorbers by polymerization or copolymerization of monomers which contain photostabilizing components or groups⁶⁶⁻⁶⁹.
3. By using photorearranging groups.

It is well known that proper selection of a photostabilizer/processing antioxidant combination can result in an overall improvement in photo and thermal stability of the formulation. It is also well known that improper selection of antioxidants for use with light absorbers can result in less than expected photostability, particularly in the case of polyolefins. Combination of UV stabilizers to achieve positive effects in photostabilization of polyolefins has become a significant method applied by industry. It is sometimes possible to combine two different types of absorbers that function by different stabilization mechanism, such as an UV screener and an energy quencher, to achieve synergism. The result is a significant improvement in the overall photo-thermal-stability. In all combinations the system to be used must be thoroughly investigated and extreme caution must be taken. It is possible that chemical interaction between additives can result in unwanted side effects and possible elimination of the desired advantages⁷⁰.

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